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HYDROGEN STORAGE AND TRANSFER

STEVENS INSTITUTE OF TECHNOLOGY

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Various modes of hydrogen storage are considered: compressed gas, liquid and solid (Hydride). Preliminary analysis of energy-storage densities and costs dictated more detailed consideration of hydrogen storage as a cryogenic liquid or metal hydride for 1) small-scale mobile storage and 2) large-scale stationary storage. Concentration was on these two modes in gathering and evaluating sufficient quantitative information to allow assessment of (cont'd)

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engineering problems and overall practicality.

Liquid-hydrogen liquefaction, transfer and storage, and safety were explored. Storage and transfer of liquid hydrogen appears sufficiently unattractive that it may not prove practical in a large number of applications. Liquefaction-energy requirements and costs are high; handling and transfer-line cooldown presents control and mechanical-integrity problems; and a liquid-hydrogen spill in an enclosure represents a significant fire and explosion hazard.

Liquid-cryogen pumping technology is reviewed with particular concern for application to airborne pumping of liquid-hydrogen. Pump types and performance are examined and technical problems identified. Further R & D is suggested.

An examination of the state -of-the-art of metallic-hydride hydrogen storage is examined. Technical problems are identified. The characteristics of present systems and their implications are discussed.

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Dr. Richard B. Cole
201-792-2700, Ext. 254

Scientific Officer: Director, Power Programs
                                Materials Sciences Division
                                ONR, Department of the Navy
                                800 North Quincy Street
                                Arlington, Virginia 22217

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iii

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

TECHNICAL PROBLEM

The work reported here is part of a larger effort concerning the possible large-scale use of hydrogen as a fuel and aimed at (1) identifying and defining the technical problems associated with such use, and (2) indicating solutions or approaches to solving such problems. At its initiation in January 1974, the program was to cover hydrogen production, storage and handling, and energy conversion. During the program, hydrogen production was deemphasized by mutual agreement. This Semi-Annual Technical Report is in two volumes; Volume I dealing with hydrogen storage and transfer and Volume II which will deal with hydrogen energy conversion. The intent of these is to provide documentation for much of the program's Final Technical Report. Therefore, the present volume of the semi-annual report emphasizes problem identification rather than solution. The final report will emphasize synthesis and a broader viewpoint in treating hydrogen-use problems and solutions.

GENERAL METHODOLOGY

The present report derives from an overview of promising alternatives for storage (Section 1) and focusses concern on (1) cryogenic liquid-hydrogen (LH_2) storage and transfer and (2) metallic-hydride storage. These areas were examined in detail as appropriate to their disparate levels of current development. The technology of cryogenic-hydrogen storage, being substantially developed industrially, was investigated largely by means of the extensive literature on the subject. In contrast, the technology of hydride storage is much less developed and was investigated largely through personal contacts with workers in the field as well as through the published literature. During the interim between this report and the final program report, additional results, e.g., those of active current efforts, will be factored together with the current results as an expanded data base for the synthesis comprising the Final Technical Report.

TECHNICAL RESULTS

For large-scale hydrogen storage, cryogenic and hydrided forms of hydrogen can be identified as the most-likely candidate storage modes on the basis of the amount of energy stored per unit volume and/or weight. For small-scale, portable storage, both hydride and cryogenic hydrogen are of promise for some situations, e.g., for land vehicles. In other situations, e.g., marine and air vehicles, only the cryogen is attractive. Cost data also support these candidates, though hydride-storage costs are not well documented. Organic hydrogen-carrier compounds ("non-metallic hydrides", e.g., methyl-cyclohexane) have not currently been investigated enough to assess well as potential hydrogen-storage means.

Currently, liquid-hydrogen storage suffers from liquefaction costs which exceed current costs of gaseous hydrogen by factors of two or three. Even if, in the future, gaseous hydrogen is not produced from low-cost natural gas and refinery off-gas, liquefaction costs are likely to be comparable with gaseous-hydrogen costs. High cryogen losses during storage and transfer also detract from LH_2's viability, a fact not widely exposed (Section 2.3.4). Finally, the possibility of cryogen spillage or leakage poses a safety (e.g., detonation) problem, especially in confined quarters (Section 2.4.1). It is concluded that, although cryogenic hydrogen is apparently the only feasible choice for some specific applications (e.g., aircraft), those applications demanding low cost and high overall energy efficiency will not attract the use of cryogenic storage (Section 2.5).

For the future, hydrogen liquefaction efficiency and steady-state cryogenic storage and transfer losses do not appear as high-promise areas for research and development owing to their relatively high current state of development. On the other hand, decreased transient losses in storage and transfer could be developed. Cryogenic equipment such as pumps (Section 3) will need substantial development before cryogenic hydrogen can be handled consistent with the weight, reliability and performance demands of, for example, aircraft applications (Section 3.3).

Metallic-hydride storage of hydrogen is still in its infancy and, therefore, provides less basis for identification of real rather than hypothetical problems. To date, hydrides have appeared

that are comparable with liquid hydrogen in hydrogen energy stored
per unit volume but at much higher weight (e.g., 50 times heavier).
This weight penalty is the major problem with current hydride
compositions and offsets some of the hydrides' advantages relative
to LH_2, e.g., lower anticipated operating cost. The weight problem
has provided the impetus for current searches for more effective
hydride compositions. Hydride-system capital costs are currently
high but probably due in large measure to limited attention thus
far.

Several potential technical problems with hydrides are
currently unresolved but are under investigation by workers in the
area: heat transfer, deterioration and safety. Long term materials
compatibility and the need for hydrogen gas compressors are additional
problems. While none of these appears as an overriding technical
problem, heat transfer problems may be fundamentally restrictive.
Further investigation of the practicality of providing sufficient
heat transfer to and from a bed of hydride in order to absorb
and desorb requisite quantities of hydrogen gas is warranted; very
few data exist in this area. Heat transfer may ultimately determine
the practical weight, size, and reliability penalties to be paid
with hydrides, particularly in applications demanding high rapidly
fluctuating rates of hydrogen recovery from storage. Data from
current, incomplete work in this area will be factored into the
final reporting on hydrogen storage.

IMPLICATIONS FOR FURTHER RESEARCH

Held for Final Technical Report.

SECTION 1 - INTRODUCTION & SCOPE

by R.S. Magee

Hydrogen is receiving increased attention as a potential, highly flexible energy medium of the future. It is ecologically attractive, broadly usable, and it can be produced from a virtually inexhaustible feedstock, i.e., water. Much has already been written about the long-range potential for the "hydrogen economy".

Like any intermediate energy form, hydrogen requires a storage and transfer capability. This allows production facilities to operate at a constant rate while consumption rates vary considerably both on a daily and seasonal basis.

The three physical states of matter: gaseous, liquid, and solid, form a convenient means of classifying hydrogen storage systems. A comparison of the likely short-and-intermediate-term hydrogen-storage alternatives is shown in Table 1-1 along with comparable data for gasoline, as a reference. Other alternatives such as slush and solid forms of pure hydrogen are not shown owing to the fact that energy densities and production costs for these forms are only modestly different (e.g., 15-25%) from comparable data for liquid hydrogen (Ref.3). Other more exotic possibilities such as atomic hydrogen are not shown because of their relatively undeveloped technologies. These forms will be dealt with, to the limited extent that available information warrants, only in the synthesis planned for the Final Technical Report of the subject contract.

Table 1-1 indicates approximate energy-storage densities (BTU/lbm and BTU/ft^3) for the fuel alone in the various physical states, as well as approximate energy-storage densities for fuel in existing storage vessels. Also shown in Table 1-1 are capital costs ($/10^{6}BTU) for selected storage capacities in the three physical states. Criteria other than those shown in Table 1-1 are relevant in particular cases; safety, reliability and maintenance, hardenability, ease of use, limits on storage duration, etc. can be important in specific cases, particularly military ones. Nonetheless, the data shown are useful in making preliminary comparisons of the relative feasibility of the various storage methods in particular applications.

TABLE 1-1: COMPARISON OF VARIOUS HYDROGEN-STORAGE MODES AND HYDROCARBON REFERENCE							
Fuel	Selected** Fuel Storage Capacity		Capital Cost [from Ref. 1] (1972 $/$10^6$ BTU)	Approximate Energy Storage Density			
				BTU/lbm		BTU/ft^3	
	10^6 BTU	ft^3		Fuel Only*	Fuel & Vessel+	Fuel Only*	Fuel & Vessel+
Gaseous H_2 2,400 psig tank	2 50	46 1140	750 720	51,600	1,200	43,800	40,000
Liquid H_2	2 50 36,000	8.8 220 158,000	1,000 300 26	51,600	8,000	230,000	130,000
H_2 as Metal Hydride FeTiH$_2$++ Mg$_2$NiH$_4$	0.72 2	4.3 12	12,000 -	980 1,860 (incl. hydride)	580 -	200,000 170,000 (incl. hydride)	140,000 -
H_2 as "Non-Metallic" Hydride Methylcyclohexane (C_6H_{11}-CH_3)	2	13	-	3,200 (incl. hydride)	-	150,000 (incl. hydride)	-
Hydrocarbon Reference Gasoline (C_8H_{18})	2 50 1,370,000	2.4 60 1,640,000	15 2 0.4	19,100	15,000	835,000	830,000

*Based on:	Density(lbm/ft^3)	%H$_2$(wt.) available
H_2	4.43(liq.)	100.
Gasoline	43.8	15.8
FeTiH$_2$	206.	1.89
Mg$_2$NiH$_4$	90.	3.6 } Not currently operational
Methylcyclohexane	48.	6.12 }

**Capacities selected to coincide with available cost and energy density data.

+Typical values from existing units.

++From Brookhaven Nat. Lab. Unit supplied to PSE&G Co. (Ref. 2). Cost calculated from formula (Ref. 3).

All current and currently proposed methods for the production of hydrogen result in gaseous hydrogen rather than a liquid or a hydride. Thus, since hydrogen will be produced and ultimately used as a gas, it might seem advantageous to store and transmit hydrogen in the gaseous form.

Results from recent studies indicate that the storage of gaseous hydrogen in pressure vessels appears to be "hopelessly non-competitive" with other alternatives over the full range of storage capacity (Ref.1). This is due to two factors: the low density of gaseous hydrogen even at high pressures, and the high cost of the pressure vessel. These factors cause compressed-gas storage of hydrogen to be bulky and/or heavy and capital cost per unit of stored chemical energy (e.g., $/10^6$ BTU) to be high for gaseous hydrogen. Furthermore, economies of scale are very modest.

There are specific, typically small-scale situations, for which compressed-gas storage of hydrogen might be warranted and is presently used. For example, hydrogen-gas tank trailers are currently in use, though the quantities handled are small. However, for the reasons cited, large-scale hydrogen use does not appear likely to involve storage in pressure vessels.

Bulk hydrogen fuel could be supplied by gas pipeline. Thus, the hydrogen would be distributed in the same form as it is produced and eventually used; and the pipeline could serve as an inventory device (line packing). Such an approach is used in the Ruhr-Valley hydrogen pipeline of 130 miles length in West Germany (Ref. 4). For example, a 2-ft. diameter, 300 mile long transmission line holding hydrogen at 1000 psia would <u>store</u> 1.7×10^6 lb H_2 (9×10^{10} BTU). "However, line-packing will probably be unimportant as a storage technique for hydrogen" (Ref.5). Line-pack storage can only meet daily needs; seasonal peak-shaving requirements must be satisfied by large-scale storage containers (natural or fabricated).

It may be feasible to store large quantities of gaseous hydrogen underground in mined caverns, aquifers, depleted oil and gas wells, or in bladder devices. For example, an aquifer storage system at Baynes, France, with a capacity of 7×10^6 ft^3 at 570 psia, has been in operation for over ten years, initially with manufactured gas and currently with natural gas. Economically, these approaches

-6-

seem promising. Reference 1 cites a capital cost of $3-6/10^6 BTU for large underground storage in aquifers, and $350/10^6 BTU for storage in a 866,000 ft^3 mined cavern at 900 psig. However, more work must be done to establish the feasibility of these various approaches with hydrogen and the ultimate potential for their employment.

Thus, if gaseous hydrogen is to be stored and transmitted on a large scale, the only practical means seems to be storage in large natural underground reservoirs and transmission by pipeline.

Cryogenic technology has made significant advances as a result of the large use of liquid hydrogen in the aerospace industry over the past 25 years. There is little doubt as to the feasibility of employing hydrogen as a liquid; however, high lique-faction energy requirements and costs, coupled with evaporation and transfer losses, raise serious questions as to the economic practical-ity of this approach.

Hydrogen can also be stored by chemically combining it with various metals to form hydrides. The formation of the hydride is accompanied by the release of heat; when the hydride is reheated, the hydrogen gas is evolved. Hydrides are attractive since hydrogen gas can be stored in solid form at room temperature at a volumetric energy storage density equal to or greater than that of liquid hydrogen. However, because hydrogen is combined with metal elements that are of comparatively high atomic weight, the weight energy-storage densities (BTU/lbm) of hydrides are low, making them unattractive at present for mobile applications. Thus, while the concept of hydride storage is appealing for stationary applications, mobile applications will probably require hydride materials of lighter weight than those currently being considered.

Recent attention has been focused on the feasibility of storing hydrogen in "non-metallic" hydrides (Ref.6). Of several possibilities, one such scheme, the catalytic dehydrogenation of methylcyclohexane to toluene, significantly increases the fuel weight energy-storage density over that of currently considered metal-hydride systems. Work in this area is just beginning, and it is too early to assess adequately the feasibility of this approach. Initial indications are that volumetric energy density is a substantial problem as is weight, especially if the necessary processing equipment is charged to the storage system. The energy balance of the process is also

-7-

reportedly not favorable, requiring for example, that some hydrogen be burned to provide process heat in addition to waste-heat recovery.

This report explores two forms of hydrogen storage and transfer: liquid and solid (in the form of metal hydrides). If hydrogen is to be considered as vehicle or aircraft fuel, small-scale mobile storage is required. The above two storage forms seem to warrant consideration for these applications. Also, large scale stationary storage of hydrogen might utilize either of these approaches, say, for seasonal or daily peak-shaving, especially when large underground storage areas are not available. The goal of this study is to develop sufficient quantitative information on which assessment of the engineering problems and overall practicality of these two approaches can be based.

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SECTION 2 - LIQUID HYDROGEN

by R.S.Magee

2.1 - INTRODUCTION

Cryogenic technology has undergone significant advances as a consequence of the large use of liquid hydrogen (LH_2) in the aerospace industry over the past 25 years. A considerable commercial business has been established to liquefy, transport and store large quantities of hydrogen. Therefore, there is little doubt as to the feasibility of employing hydrogen as a liquid. Criticism of this approach has focused primarily on the question of economic practicality.

A liquid-hydrogen fuel system requires a safe, economical series of processes to liquefy, distribute, store, and finally deliver liquid hydrogen to the user. Current liquefaction technology is well advanced and presents no major problems. However, the capital costs and energy expended for liquefaction significantly increase the cost over that of gaseous hydrogen. Recently, attention has been focused on various schemes to recover a portion of this liquefaction energy, but opportunities for recovering a large portion are very limited.

The transfer of liquid hydrogen through lines from one container to another is inherently wasteful. Large amounts of hydrogen gas are generated when liquid hydrogen boils to cool transfer lines and storage vessels from initial ambient temperature. If not recovered, this gas can represent a significant loss; and when vented to the atmosphere, it may also represent a fire hazard. Nevertheless, batch transport of hydrogen as a liquid has often proved to be more economical than transport as a gas.

Hydrogen as a liquid fuel has certain obvious advantages: relatively high density, ability to absorb large quantities of heat as its temperature is raised, and low-pressure (low-weight) containers. Some of these properties of liquid hydrogen are shown in Table 2-1 below. However, liquid hydrogen is not without its disadvantages as well: theoretical and practical thermodynamic inefficiencies, transfer losses, chilldown losses, steady-state boil-off losses, and the potential for a large fire from a small liquid-

TABLE 2-1: PROPERTIES OF LIQUID HYDROGEN*

Normal boiling temperature	36.7°R
Critical temperature	59.74°R
Critical pressure	12.98 atm
Density	4.43 lbm/ft^3
	0.59 lbm/gal
Heat of vaporization	191.9 BTU/lbm
	113.7 BTU/gal
Sensible heat	
saturation temp. to 540°R	1710. BTU/lbm
saturation temp. to 1460°R	5500. BTU/lbm

*For composition in equilibrium at 70°F (25% para, 75% ortho)

hydrogen spill.

It is the purpose of this section to explore various aspects of liquid-hydrogen liquefaction, transfer and storage, and safety with the goal of developing adequate quantitative information on which an assessment of the engineering problems associated with a total liquid hydrogen system can be based.

2.2 - LIQUEFACTION

Hydrogen is typically produced as a gas. The production of liquid hydrogen requires additional capital investment, energy expenditure, and plant operating costs. In this section, an estimate of these costs is presented for liquefaction plants of various sizes.

As a context in which to view these costs, current hydrogen-gas production costs can be cited. Most industrial hydrogen today derives from natural gas or petroleum-refinery gases. From natural gas, hydrogen costs about 0.045 to 0.07 $/lb (0.9 to 1.4 $/BTU). As energy sources for hydrogen production from water, coal and electricity are higher-cost alternatives, increasing hydrogen production costs to 5-6 $10^6 BTU in the case of electricity at 12 mills/KW-hr.

2.2.1 - Energy Requirements

The minimum work requirement (ideal work of liquefaction) to liquefy gaseous hydrogen from 70°F and 1 atm to saturated liquid at 1 atm is 5002 BTU/lbm (Ref.1). Strobridge (Ref.2) has published

a survey and correlation of current refrigerator/liquefier capital costs and energy requirements. Parrish and Voth (Ref.3) have used these data to determine the efficiencies for various-sized units. The efficiencies shown in Table 2-2 were based on existing plant operations (the largest existing plant is approximately 7,700 lb/hr) with a reasonable extrapolation to a 40 per cent efficiency for a 220,000 lb/hr plant. Also shown in Table 2-2 are the liquefaction energy requirements for the different sized plants.

TABLE 2-2: PRACTICAL ENERGY REQUIREMENTS FOR PRODUCING LIQUID HYDROGEN FROM GASEOUS HYDROGEN

Plant size, lb/hr	Liquefaction efficiency, %	Practical energy requirements, BTU/lb
220,000	40	12,500
15,000	35	14,300
7,700	34	14,700
3,300	33	15,200
1,100	30	16,700

Thus, it requires 24 to 33 per cent of hydrogen's lower heating value (51,600 BTU/lbm) to convert it into liquid.

2.2.2 Capital costs

Strobridge's survey of current refrigerator/liquefier capital costs yielded the following correlation:

$$C = 6000P^{0.7}$$

where C = capital investment cost in 1973 dollars

P = installed compressor power, kilowatts

Parrish and Voth used the above equation to calculate the capital investment costs shown in Table 2-3.

These costs reflect one-of-a-kind construction, and large scale construction of liquefaction plants could lead to modular design and lower costs.

2.2.3 Liquefaction Costs

In order to determine the cost of producing liquid hydrogen,

TABLE 2-3: CAPITAL COSTS FOR PRODUCING LIQUID HYDROGEN FROM GASEOUS HYDROGEN (1973 Dollars)	
Plant size, lb/hr	Cost, $
220,000	94.6×10^6
15,000	16.2×10^6
7,700	10.1×10^6
3,300	5.7×10^6
1,100	2.8×10^6

the cost of the required power, the operating and maintenance costs, and the fixed charges on the capital investment must be added. Using a power cost of 12 mills/kw-hr, a 90% plant-use factor, a 15% interest rate and a 25-year plant life, Parrish and Voth have calculated the liquefaction costs shown in Table 2-4.

TABLE 2-4: LIQUEFACTION COSTS (1973 Dollars)		
Plant Size, lb/hr	Cost, $/lb	Cost, $/10^6 BTU
220,000	0.068	1.32
15,000	0.098	1.90
7,700	0.110	2.13
3,300	0.127	2.46
1,100	0.166	3.22

The costs shown in Table 2-4 are based on current technology and extrapolations of trends in efficiency.

2.2.4 - Recovery of Liquefaction Energy

As indicated above the energy and cost requirements to liquefy hydrogen are significant and are a deterrent to the use of liquid hydrogen as an energy carrier. However, when gaseous hydrogen at ambient temperature and pressure is desired and liquid hydrogen is available, it is possible to recover some of the liquefaction energy.

The maximum amount of energy that can be recovered in obtaining gaseous hydrogen (STP) from liquid at 1 atm is the _ideal_ work of liquefaction - 5002 BTU/lb, or 10% of hydrogen's lower heating value. A practical process of reconversion to mechanical work might recover one third of this energy, resulting in an overall recovery of about 12% of the _actual_ work of liquefaction or only 3% of hydrogen's lower heating value. While small as a percentage, this could yield a significant amount of recoverable energy in large systems. Still, in light of the low efficiency, it appears that benefit must be gained from the low temperature of cryogenic hydrogen beyond that deriving simply from its availability as a heat sink for heat-engine operation.

2.2.5 - Parahydrogen

Hydrogen can exist in two different molecular forms: ortho-hydrogen and para-hydrogen. The difference between these two forms of hydrogen is the relative directions of spin of the nuclear particles which make up the hydrogen molecule. The relative concentrations of these two forms at equilibrium is strongly temperature dependent.

The liquefier efficiencies presented in the previous section were based on the production of parahydrogen. Hydrogen in equilibrium at 70^OF and 1 atm is 25% parahydrogen and 75% orthohydrogen. On liquefaction in the absence of a catalyst, the liquefied hydrogen retains this composition. However, the mixture undergoes a slow conversion to an equilibrium composition at 36.7^OR of virtually 100% parahydrogen. This involves an exothermic reaction of second order with respect to the orthohydrogen concentration. This conversion is not instantaneous but takes place over a period of time because the change involves energy exchanges by molecular magnetic interactions.

If the unconverted normal hydrogen is placed in a storage vessel, the heat of conversion (304.8 BTU/lbm) will be released in the vessel. Since the latent heat of vaporization is 191.9 BTU/lbm, significant boil-off of the liquid occurs due to ortho-para conversion. The extent of this storage loss, for a perfectly insulated vessel, is shown in Fig.2-1. The high initial boil-off rate

-13-
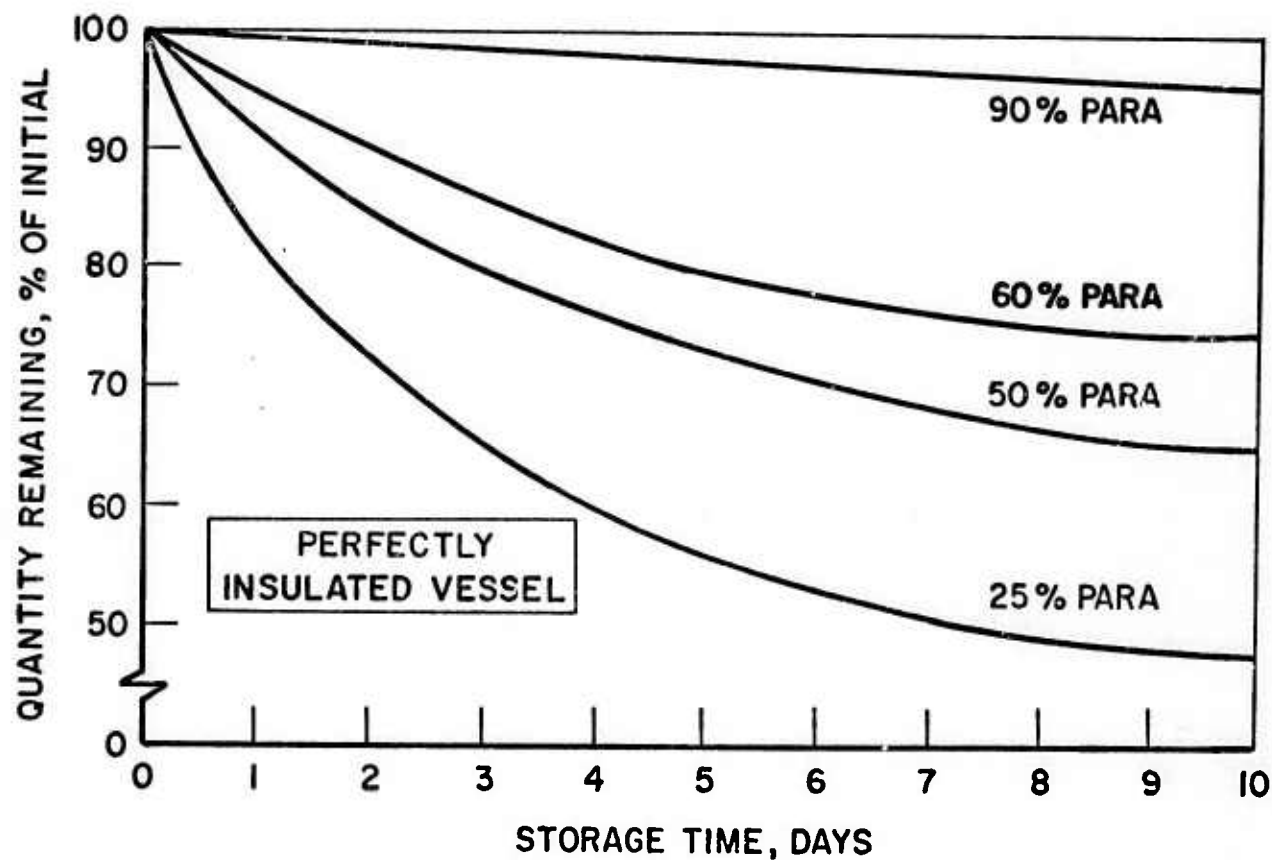
FIGURE 2-1: LIQUID HYDROGEN STORAGE LOSSES FOR VARIOUS
INITIAL PARAHYDROGEN CONCENTRATIONS
(Ref.4)

of 25% para ("normal") hydrogen implies a need for either venting, vapor storage or reliquefaction if the initial boil-off vapor is not usable at a rate of about 20% per day.

Therefore, when the vessel to be filled is large (necessitating a long production period), or when there may be a delay between production and use, a catalyst is employed to speed up the conversion so that the energy is removed during the liquefaction process rather than while the liquid is stored. However, conversion to parahydrogen reduces the liquefier output - about 35% if conversion of normal hydrogen to parahydrogen is done at 36.7^OR. (Similarly, if vapor phase conversion to 60% parahydrogen at liquid nitrogen temperature is used prior to conversion at 36.7^OR to 100% parahydrogen, the liquefier output is only reduced by about 23%).

Thus the question arises as to whether this conversion is justified at the expense of reducing the liquefier output.

For most practical applications, relatively long storage is unavoidable for user and supplier. Under this condition, production of 100% parahydrogen is advantageous unless most of the boil-off caused by ortho-para conversion can be used as vapor. However, some situations require high output for immediate use, and then it is advantageous to increase the liquefier output at the expense of the parahydrogen concentration of the liquefied product.

For example, since the production of 100% parahydrogen from normal hydrogen (25% parahydrogen) typically results in about a 23% decrease of liquefier output, Fig.2-1 indicates that when the liquefied product is stored in perfectly insulated vessels, conversion to 100% parahydrogen is justified only when storage beyond 1 1/2 days is anticipated. Thus a knowledge of liquefier output versus per cent of parahydrogen in the liquefied product allows optimization of a liquid hydrogen production and storage system for a specific mission.

2.3 - STORAGE AND TRANSFER

Once cryogenic hydrogen has been liquefied and then purified to the required level, a transfer and storage system is required. The primary objectives of any cryogenic storage and transfer system are to minimize cryogenic fluid losses and maintain the desired transfer rates, with a system that is economical, reliable and safe.

The design of cryogenic-hydrogen storage vessels and transfer lines progressed rapidly during the space program. It is not the intent here to provide the means to design such systems, but rather to point out some of the operating difficulties of such systems and to present available data from actual operating experience. Differences between the transient (or start-up) behavior of these systems and their steady-state characteristics are major considerations.

2.3.1 - Representative Storage and Transfer Losses

Losses during handling and transfer are significant, and it is not difficult for large quantities of liquid to be lost when improper handling techniques are used. Some general experience data support this point.

At a liquid-hydrogen plant operated by Air Products, Inc. in Painesville, Ohio, 85% of the liquid produced is shipped and 15% is lost during handling at the plant; while at another plant in West Palm Beach, Fla., losses amount to less than 10% of full capacity (Ref.6). NASA has gathered data on liquid-hydrogen usage and losses in the space program (Ref.7). 460,000 gal. of liquid hydrogen are supplied to fill the Saturn V vehicle for launch. Since the second and third stages of the Saturn V vehicle have capacities of about 270,000 gal. and 73,000 gal. respectively, transfer losses of 117,000 gal. or 25.5% of the total are apparent. Finally, experience at the Los Alamos Scientific Laboratory obtained while handling liquid hydrogen in 5500-liter (1450 gal.) batches, indicated that losses during transfer from the transport Dewar to a similar stationary Dewar amount to 10 to 20%, depending critically on the temperature of the receiving Dewar (Ref.8). This handling and transfer experience with liquid hydrogen is summarized in Table 2-5.

The data shown in Table 2-5 indicate losses from only one portion of the particular liquid-hydrogen system referenced. Of greater interest would be the total losses at a typical facility due to the handling, transfer and storage of liquid hydrogen. The author was unable to locate such information. However, for comparison, it is useful to review early experience with liquid-oxygen (LOX) losses at Edwards Air Force Base (Ref.9). A detailed review of

TABLE 2-5: LH$_2$ HANDLING AND TRANSFER EXPERIENCE

OPERATION	SCALE	LOSS
Liquefaction plant (Ref.6)	3/4 ton/day (Ohio)	15%
	30 ton/day (Fla)	10%
Saturn V launch (Ref.7)	460,000 gal.	25.5%
Los Alamos batch transfer (Ref.8)	1450 gal.	10-20%

of LOX records indicated the enormity of the liquid-oxygen boil-off losses. As much as 6.8 gallons of LOX was purchased for every gallon of LOX used in a rocket firing, i.e., a loss of 85.3%. A detailed analysis indicated the origins of these losses. LOX was obtained at a nearby railway depot. Liquid oxygen was unloaded from a railway tank car, transferred by gas pressurization through a flex hose, filter, valves, flanges and piping, transported 30 miles to the test stand site, and rapidly unloaded by gas pressurization and a pump through a complex network of metal piping that required chilldown. During this transfer, 13% of the liquid oxygen boiled away. This loss is attributed to the gas pressurization, chilldown of transfer lines, heat leak through surfaces, liquid trapped in the transfer line (and eventually drained at the end of each operation), and leakage. The remaining losses occurred at the test-stand site. A summary of the losses is shown in Table 2-6. About 50% of the liquid oxygen is lost aside from missile-tank heat leak.

These figures are for an early liquid-oxygen experience but, similarity of the transfer losses (13%) with those of Table 2-5 for hydrogen suggests similarity of LOX and LH$_2$ losses.

2.3.2 Storage Dewars

Liquid-hydrogen storage vessels have been built that range in size from 1-liter laboratory flasks up to 850,000 gal. Dewars

-17-

TABLE 2-6: LOX LOSSES AT EDWARDS AIR FORCE BASE (Ref.9)

Operation	LOX Loss
Transfer from railroad car to base storage vessel	13%
Transfer from storage to missile (chilldown)	8%
Missile-tank chilldown	13.7%
Liquid trapped in transfer system	14.5%
External heat-leak during storage and hold	36.1%
Total	85.3%

used to store hydrogen for space applications. The performance of these storage vessels varies and depends primarily on the type of insulation employed, vessel size and shape, and vessel structural-support considerations. In this section, some of the parameters which affect hydrogen storage-vessel design are considered. Also of interest is the performance of existing Dewars (e.g., boil-off losses, chilldown losses, energy-storage density, etc).

2.3.2.1 - Insulation

The past two decades have seen marked improvement in thermal insulations for cryogenic-hydrogen applications. In fact, material development and insulation concepts have advanced beyond our ability to optimize their use in engineering design, since heat loss through supports, ports and piping is significant. The proceedings of past Cryogenic Engineering Conferences (Ref.5) document insulation-technology development.

Insulations frequently used for the storage of liquid hydrogen are: vacuum with a liquid-nitrogen shield; evacuated foams; evacuated perlite; and evacuated multi-layer "super-insulations". The choice of insulation for a particular application is usually a compromise in which such factors as cost, ruggedness, weight, volume, and reliability are considered along with the insulating properties of the material.

Insulating properties are typically reported as an apparent thermal conductivity, even though the heat flux per unit area is a result of the combined conduction, convection and radiation heat flux. A summary of these results is shown in Figure 2-2.

For a given design heat loss, the required insulation thickness can vary greatly depending on the type of insulation chosen. For example, the 26,000 gal. storage tank frequently employed for rail shipments, contains a 15-inch thickness of perlite insulation, and the hydrogen loss rate is approximately 0.5% per day. Since hydrogen transport vessels are typically volume limited rather than weight limited, Perkins and Frainier have calculated that by retaining the vessel's outside dimensions and decreasing the insulation thickness to maintain the same performance with Linde SI-4 super-insulation, the storage tank capacity may be increased from 26,000 to 35,000 gal. (Ref.10).

In addition to thermal effectiveness and volume considerations, weight of the required insulation may be a consideration. The densities of the various insulation materials are shown in Table 2-7.

TABLE 2-7: DENSITY OF CRYOGENIC INSULATIONS	
Material	Density lb/ft^3
Polystyrene foam	2 - 3
Fibreglas	0.5 - 10
Perlite powder	5 - 6
Super-insulation (Linde SI-4)	4.7

Insulation weight is important not only to total container weight, but also to cooldown losses; the larger the mass of insulation, the greater the storage vessel cooldown loss. As an example, Ishaghoff and Canty (Ref.11) have calculated that it would require 109,000 lbs of perlite to reduce the steady-state boil-off loss from a 105,000 gal. (62,200 lb) liquid hydrogen tank to 0.3%. The cooldown loss for this 109,000 lb of perlite would amount to 24,900 lb of liquid hydrogen or 40% of that stored. On the other hand, 1050 lb of quilted super-insulation would yield the same thermal performance
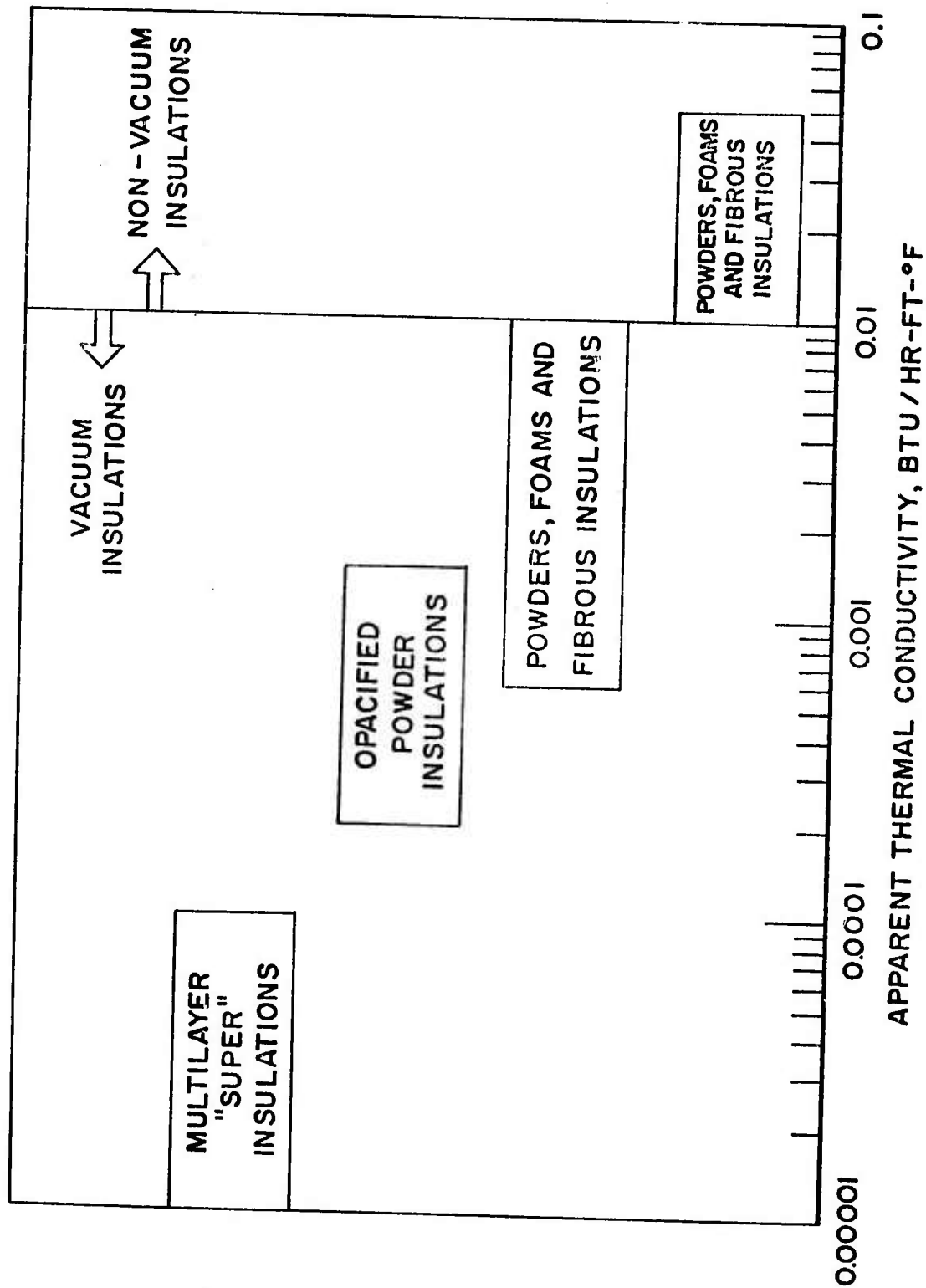
FIGURE 2-2: APPARENT THERMAL CONDUCTIVITY
OF CRYOGENIC INSULATIONS

and the cooldown loss would only be about 240 lb or 0.4% of the stored hydrogen. Consideration of cooldown loss may control the design in instances when the storage Dewar is frequently emptied and later re-filled. In such a case, vacuum insulation alone might be the best choice since it minimizes the cooldown loss.

The material cost per unit volume for expanded foams, powders and fibrous materials is low. The cost per unit volume for the super-insulations, on the other hand, is high. However, since less material is required for equal performance, the cost of the insulation for a given container makes the choice of super-insulation attractive in some applications (generally smaller Dewars with large surface-to-volume ratios). Stoy (Ref.12) has shown that while the installed material cost of super insulations are nearly 90 times that of per-lite on a unit-volume basis, the total insulation cost for the same steady-state thermal performance is only 4 times higher, owing to the smaller volume of super-insulation required.

The practical performance of these different insulations varies. Expanded foams have the disadvantage that their large thermal-expansion coefficients can cause cracking in the foam during cooldown, while diffusion of H_2 gas into the voids can increase the thermal conductivity by a factor of 3 or 4. Evacuated powders may pack under vibrating loads and thermal cycling, increasing the heat flux. In evacuated powders the residual gas pressure must remain below 10^{-2} torr to achieve low apparent thermal conductivity. The multilayer super-insulations suffer for two reasons. They must be evacuated to pressures below 10^{-4} torr to be effective. They are also difficult to apply to complicated shapes. These practical performance factors must be considered when evaluating insulations for a specific application.

2.3.2.2 - Steady-state Performance

Design of a stationary liquid-hydrogen storage tank frequently resolves itself into balancing initial cost against boil-off rate. For transport Dewars, weight, volume, and ruggedness also become a design consideration. It is therefore useful to be able to make a rough estimate of the insulation requirements imposed by a given evaporation rate.

However, heat loss from liquid-hydrogen storage tanks is not

-21-

restricted to heat flux solely through the insulation. Unfortunately in present day storage vessels, supports, ports, and piping can account for 20 - 50% of the total heat leak (Ref.12-14) depending on the container size, g-loading requirements, etc.

A means for estimating insulation requirements was developed by Perkins and Frainier (Ref.10) and is shown in Figure 2-3. Figure 2-3 shows thermal resistance (x/k) versus tank capacity for a boil-off loss of 1% per day of liquid hydrogen. This curve allows one to estimate quickly the thickness of a given insulation (x) required to satisfy a given hydrogen boil-off rate with an insulation of a given thermal conductivity (k). The curve accounts for typical heat leaks through supports and piping, and therefore, unusual tankage incorporating such factors as high "g" loadings, large man-holds, or high L/D ratios would require adjustment of the values shown.

For example, a 10,000 gal. tank might demand a loss of 1% per day. From the figure, the thermal resistance required is 1000. If an evaculated perlite insulation (k=0.0007 BTU/hr-ft-^{O}F) is to be used, the required thickness is 0.7 ft. For losses other than 1%, the thickness required is obtained by dividing the thickness obtained from Fig.2-3, by the desired loss rate in % per day. For example, with a desired loss rate of 0.1% per day, the thickness required would be 7 ft.

Current LH$_2$-Dewar Performance

Design data and operating experience have been gathered for a variety of liquid-hydrogen Dewars which range in size from 40 gal to 850,000 gal. These data are shown in Table 2-8. Boil-off loss data and some cost data are plotted in Fig. 2-4 versus tank capacity. These data indicate a rough trend for boil-off losses versus capacity; however, it is not surprising that the correlation is poor, since the vessel shape and type of insulation used varied widely. Detailed specifications for the various insulations used are not readily available so no attempt has been made to correlate subsets of the total body of data for specific types of insulation. The cost data seem to correlate surprisingly well and indicate that costs may be approximated (in 1975 dollars) from

$$C = 160 \ G^{-1/3}$$
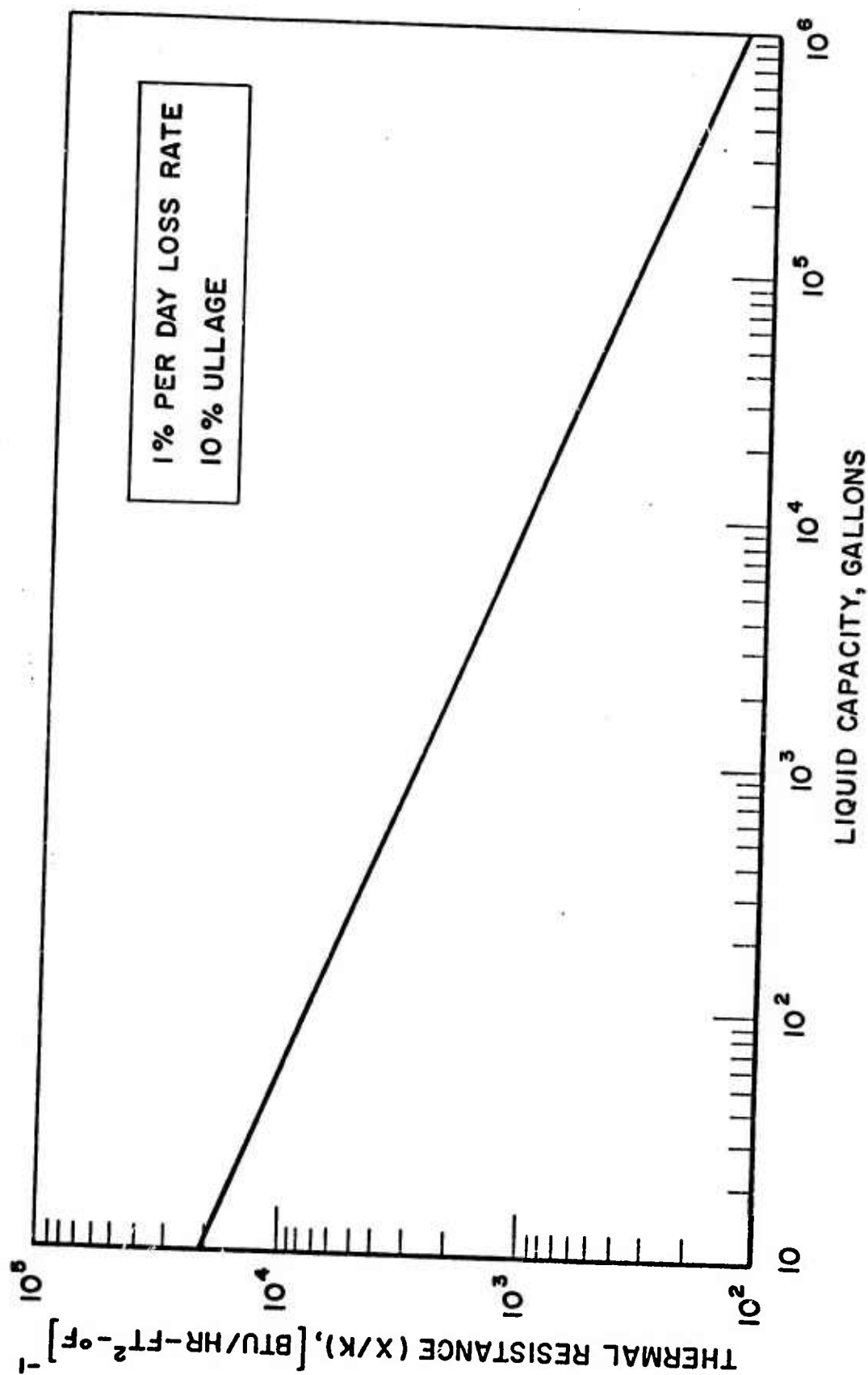
FIGURE 2-3: INSULATION REQUIREMENTS FOR TYPICAL LIQUID HYDROGEN TANKAGE (Ref.10)

TABLE 2-8: LH$_2$ STORAGE DEWAR PERFORMANCE

Dewar Identification	Capacity		Insulation	Boil-off %/day	Dewar wt,lb	Dewar vol,ft³	BTU*/lb	BTU*/ft³	Cost, $/gal (1975)
	gal	10⁶BTU*							
Linde-LSH 150 Ref.10	39.7	1.21	Linde SI-4 (1")	2.5-3.0	166	10.7	7,300	113,000	$50/gal Ref.15
Balloon Flight Ref.41	120	3.67	Evacuated Santocel	-	550	37.9	10,500	97,100	-
Linde LSH 1000 Ref.10	264	8.07	Linde SI-4 (1¼")	1.0	2,400	158	5,370	51,000	-
Beech Transport Trailer Ref.8	1,585	48.4	Powder	1.9	-	-	-	-	$12/gal
Semi-Trailer Ref.10	7,800	238	Linde SI-4	<0.5	32,200	1,780	7,400	134,000	-
Conventional Trailer Ref.7	13,000	397	Evacuated Super-insul.	0.8 0.25	40,700	-	9,700	-	-
Ref.40	14,000	428	Evacuated Super-insul.	0.22	-	-	-	-	-
Rectangular Trailer Ref.7	16,000	489	-	0.4	40,300	-	12,100	-	-
Rail Tank Ref.10	26,000	795	Evacuated Perlite	0.5	-	6,540	-	122,000	-
Nevada Ref.17	50,000	1,530	Evacuated Perlite	0.18	-	-	-	-	-
Ref.40	200,000	6,110	Evacuated Super-insul.	0.07	-	-	-	-	-
Nevada Ref.15	500,000	15,300	Evacuated Perlite	0.05	-	-	-	-	$2/gal Ref.15
KSC Ref.7,40	850,000	26,000	Evacuated Perlite	0.026 0.03	-	180,000	-	144,000	$1-2/gal Ref.15,42

*Based on Lower Heating Value of 51,600 BTU/lbm
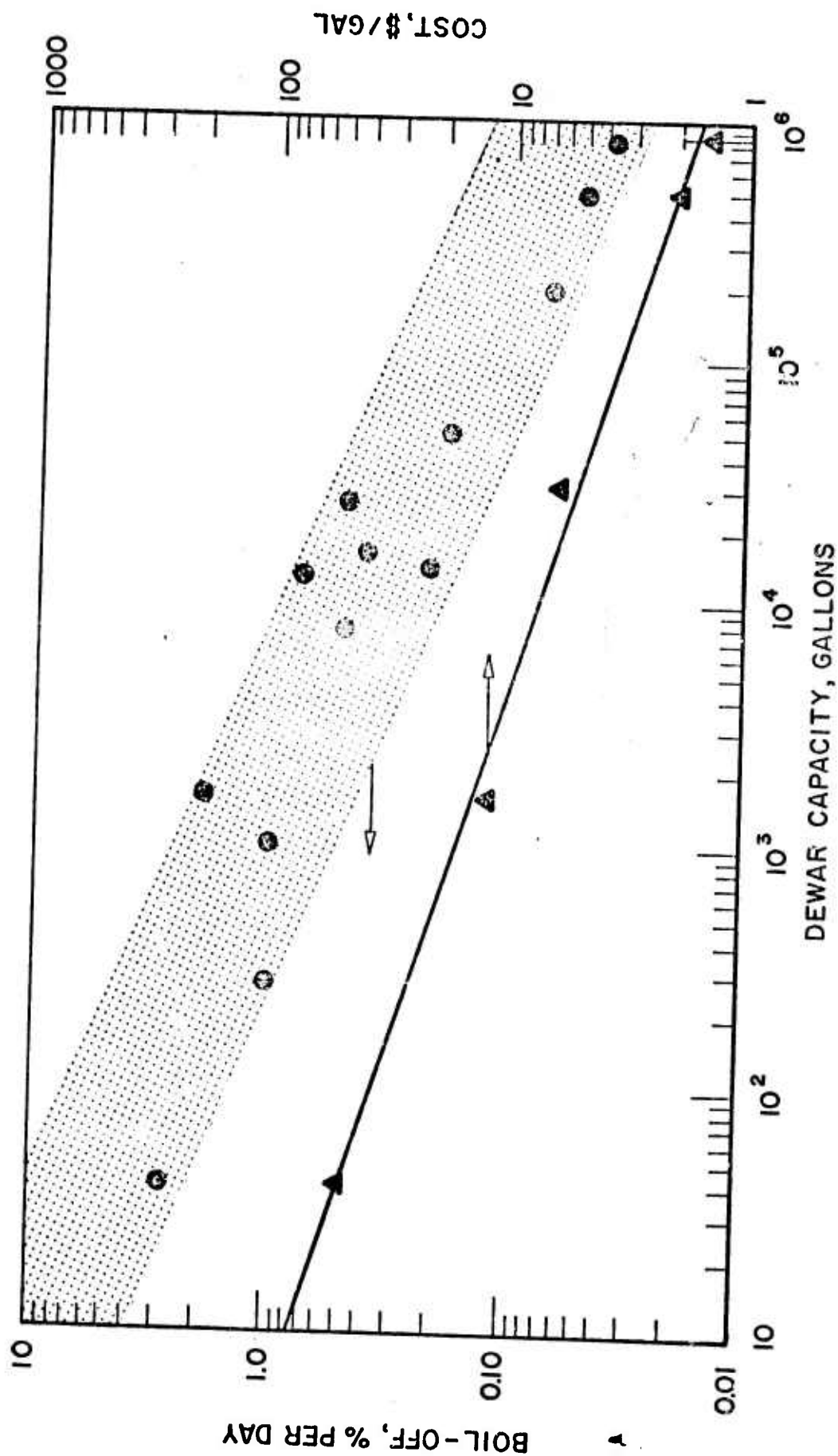
FIGURE 2-4: BOIL-OFF LOSSES AND CAPITAL COSTS FOR LIQUID-HYDROGEN STORAGE DEWARS (from Table 2-8)

where C = cost (dollars/gal) and G = tank capacity (gal.)
It should be noted, however, that the correlation reflects a small
number of data and that the costs reflect small-volume production
and are subject to substantial decreases with large volume product-
ion. A 50-gallon liquid-hydrogen storage Dewar for an auto would
currently cost about $2,500. However, manufacturers estimate prices
of from $200 to $750 based on large-volume production. (Ref.15).

Also of interest are liquid-hydrogen storage densities. Table 2-8
indicates these typically range from 97,000 - 144,000 BTU/ft^3 and
7,300 - 12,000 BTU/lbm in most existing storage Dewars. Results
from a hydrogen-tank weight optimization study for lunar storage
(Ref.16) indicated a possible storage density of 9,100 - 15,200 BTU/lbm
for storage of 75 - 150 lbm of liquid-hydrogen.

2.3.2.3 Cooldown Losses

When a liquid-hydrogen storage Dewar at ambient temperature
is filled with cryogenic hydrogen, considerable time and quantities
of liquid are required to chill the storage Dewar. In one study,
cooldown of a 50,000 gal. Dewar required vaporization of 8.1% to 16.9%
of the toal LH$_2$ supplied to fill the Dewar (Ref.17). A slow chill
was much more efficient, boiling off only about one half the liquid
hydrogen of the faster chill. Smaller Dewars, with larger surface-
to-volume ratios may require even higher percentages for cooldown.
Unfortunately, studies of Dewar cooldown and filling techniques are
very limited (Ref.17-19).

The optimum design of storage Dewars must involve the cooldown
period. In fact, in many practical instances, the heat transfer process
in the Dewar may never reach steady-state conditions. And while
the steady-state losses from a storage Dewar may always be decreased
by the addition of more insulation, this added mass to be chilled
down increases the cooldown loss.

2.3.3 - Transfer Systems

The transport of liquefied hydrogen is accomplished by either
of two methods. LH$_2$ can be transported either by batch lots in Dewars
or by continuous or intermittent flow through special piping. Some
aspects of these have already been discussed above (see 2.3.2). The
proper design of piping transfer systems is critical, especially if

transport efficiency is important and/or transfer distance long.
A number of problems arise in long lines: pressure and flow surges,
large cooldown losses, possible delays in response due to long cool-
down times, and thermal-contraction bowing of the line under partial-
fill conditions.

A major consideration for liquid-hydrogen transfer lines is the
expected steady-state heat leak through the line into the fluid.
Besides wasting liquid-hydrogen through evaporation, the resulting
two-phase flow reduces the carrying capacity of the line due both
to fluid-density decrease and to flow-resistance increase. For
example, Jacobs et al.(Ref.20) have calculated if 1% of the liquid
hydrogen evaporates in a pressurized-transfer system, the capacity
of the line falls to 6% of the design maximum flow, while if 10%
of the liquid evaporates the capacity falls to 2%. Thus, it is
advantageous to avoid two-phase flow. However, as will be discussed
later, two-phase flow during the cooldown of the pipeline is
unavoidable.

Liquid-hydrogen-transfer engineering problems are discussed
in this section, and those factors which limit the performance
of transfer systems will be emphasized. Liquid-hydrogen pumps are
discussed in a later section.

2.3.3.1 - Types of Transfer Lines

A cryogenic-fluid transfer line is generally of one of three
types: (1) uninsulated, (2) porous-insulated and (3) vacuum-insulated.
The latter may be insulated by vacuum alone or in combination with
multi-layer or evacuated-powder-insulation.

Uninsulated Lines

Liquid air, oxygen, and nitrogen are frequently transferred
for relatively short distances through uninsulated lines. Scott
(Ref.21) states "it is difficult to imagine a situation in which
an uninsulated line for liquid hydrogen would have any merit".
During transfer of liquid-hydrogen, solid air forms on the outer
surface of the line for free-convection conditions. This condensation
causes an increase in the heat-transfer rate since the latent heat
of air is transferred to the line in addition to the convection heat
flux.

Despite the short coming of uninsulated piping, Richards et al.

(Ref.22) performed a study to determine the heat-leak and pressure-drop characteristics for uninsulated liquid-hydrogen transfer lines. Their results are incorporated into single-phase flow design curves in such a way that design variables - flow rate, pressure drop, pressure, pipe diameter, pipe length, - may be related and optimum performance determined. It was concluded that the heat flux is sufficiently low to make practical the use of uninsulated liquid-hydrogen transfer lines, provided either that mass flow rates are high, the installations are temporary or experimental, or the period of use is brief and infrequent. It was also determined that the pressure drop caused by the flow of boiling liquid hydrogen could be calculated with reasonable accuracy using the correlation of Martinelli and Nelson (Ref.23) and that the pressure levels necessary to maintain single-phase flow were reasonable.

Porous-insulated Lines

Lines transferring liquid-oxygen or nitrogen are sometimes insulated by applying glass wool, polystyrene foam, polyurethane foam, etc. to bare pipes. Since water vapor degrades insulation performance, a vapor barrier is applied to the outside insulation surface. When these insulations are employed on pipes carrying liquid-hydrogen, an additional problem arises. Air condenses within the insulation, and the oxygen in the condensed air presents a fire and explosion hazard if the adjacent insulation is combustible. Consequently, porous insulations are generally not employed for liquid-hydrogen transfer.

Vacuum-insulated Lines

The most effective means of transferring liquid-hydrogen seems to be vacuum-insulated lines. These lines consist of an inner line in which the liquid flows and an outer concentric vacuum jacket. Thousands of feet of vacuum-insulated pipe have been used in the space program. Sizes have ranged from 1/4 to 20 inch diameter, pressures from a few psi to 3,000 psi, and lengths from a few feet to more than 8000 ft. (Ref.24).

The annular space may be solely vacuum, or filled with evacuated powder or multilayer insulation. Vacuum integrity is essential to maintaining thermal performance. Multilayer (radiation shield) insulation offers 1/5 to 1/30 of the heat-transfer rate of vacuum

only and also is much less sensitive to changes in vacuum level.

Evacuated powder has the advantage that the vacuum required for effective insulation is two to three orders-of-magnitude less than that required without powder (Ref.21). However, the heat capacity of powder insulation increases the cooldown losses of a transfer line. It is also difficult to avoid the formation of voids in the powder in the annular region.

Long sections of vacuum-insulated transfer line contain spacers to prevent contact between the inner and outer lines and to support the weight of the hydrogen in the line. These spacers must be designed to minimize heat leak by conduction; otherwise, the vacuum insulation becomes ineffective. Techniques for spacer design are well developed. (Ref.1).

2.3.3.2 - Design Considerations

The design of vacuum insulated piping systems requires the consideration of many factors - cost, thermal contraction effects, thermal performance, vacuum integrity, field handling and installation, and maintenance. Generally, however, the factor which requires the most consideration - once the pipe size and system layout have been determined - is adequate provision for the thermal contraction of the system.

Thermal contraction problems can be minimized in various ways:
1. Inherently flexible systems
2. Expansion joints
3. Expansion loops
4. Low thermal-expansion material (e.g., Invar)

The first three methods are frequently employed in conventional piping systems, (e.g., steam). However, because of the need for minimizing heat transfer to the liquid-hydrogen during steady-state operation and the necessity for minimizing line cooldown losses, the design of vacuum-jacketed lines for liquid hydrogen requires additional considerations. The use of Invar in cryogenic piping systems is attractive since it has a coefficient of contraction of less than 1/6 that of stainless steel at cryogenic temperatures. When fully restrained and cooled to liquid hydrogen temperature, the stress induced in Invar is approximately 10,000 psi, well below the allowable stress and an order-of-magnitude below the corresponding stress with steel. There are no general rules to follow when choosing among

these alternatives for a given system. Examples of all these approaches and combinations of these approaches are given in Ref. 24. Factors generally considered in specific cases: relative cost; pre-existence of trenches, supports and other equipment; maintenance; and reliability.

Bowing

In some instances, thin-walled transfer piping is subject to severe temperature gradients and the phenomenon of pipeline bowing occurs. Bowing is the tendency of the centerline of the pipe to be deformed into an arc. This condition occurs when the piping is only partially full of liquid, a situation common during a normal operating cycle when liquid trapped in the line between valves is allowed to boil-off, (e.g., during transfer of liquid-hydrogen to a receiver Dewar, start-up of a gas turbine, etc.). Studies with liquid-nitrogen have indicated that when the pipe is half filled with liquid, the top fibres of uninsulated stainless-steel, thin-walled pipes did not cool substantially below ambient temperature at steady-state, while the bottom fibres of the pipe were at the liquid-nitrogen temperature (Ref.25). This extreme temperature gradient causes the pipe to bow. This situation is magnified with LH_2.

The severe temperature gradient obtained in this situation can cause large additional stresses in pipes that are restrained in any manner, particularly at the support points and anchors. Therefore, unless liquid-hydrogen pipelines are properly designed for the condition of bowing, severe pipe stresses, intolerable pipe displacements, and pipe-support failures will occur.

Couplings

For long liquid-hydrogen transfer lines it is difficult to construct the line in a single section. Hence, a means of coupling sections together is necessary.

Three general types of couplings are employed. A simple connection, consisting of a bolted-flange mechanical connection surrounded with fiberglas, foam or powder insulation meets the need for simplicity and ease of maintenance; however, this type of connection imposes a large cooldown penalty and liquid-hydrogen leakage may result from improper tightening of the bolts and thermal cycling.

For applications which do not require frequent dismantling of the line, a welded joint connection is employed. This joint has the advantage of high thermal performance and low cost, at the expense of troublesome, costly disassembling methods.

A high-performance joint frequently employed is the reentrant bayonet system. It has several advantages: 1) it introduces no additional pressure drop in the system, 2) the heat leak through the joint is small, 3) the joint can be easily assembled and disassembled without special tools, and 4) there are no leakage problems with the joint. However the bayonet joint rates low in maintenance since installation requires significant axial clearance and since care must be taken not to damage the male portion during assembly and disassembly. Finally the bayonet joint is a high cost component ($900 for a 3-in x 5-in joint - 1966 price, Ref.1).

Little development work seems to be proceeding on improving the above coupling methods. However, Randall and Sullivan have developed a novel coupling concept that provides a simple, rugged, relatively low-heat-loss joint for vacuum-insulated lines (Ref.26). This coupling concept is applicable to systems needing low heat-loss joints that require easy separation for modification and/or maintenance.

2.3.3.3 Pressurized Transfer

The transfer of liquid-hydrogen from storage Dewars to points of use has been often been effected by pressurization of Dewars. Because of direct contact between the stored liquid and gas, pressurizing gas is limited to helium and hydrogen. The high cost of helium restricts its use in large systems.

The quantity of gaseous hydrogen required to pressurize and transfer a given amount of liquid is an important parameter in the selection and design of the type of transfer system to be used. The quantity of gaseous hydrogen required is dependent on the heat and mass transfer that occurs at the agitated, liquid-gas interface in the ullage of the tank. These processes are complicated, and determination of gas requirements rests largely on correlations of experimental results.

Unfortunately, there is little experimental data available on which to make such a correlation. In one study (Ref.27), eight

transfers of liquid-hydrogen were effected with pressures up to 100 psig and at rates between 31 and 560 gpm while initial and final ullages were also varied. The results showed a pressurized-gas requirement of about 1% of the mass of liquid transferred at 50 psig and 2% at 100 psig. A preliminary analysis of the process also indicated that not all of the liquid is transferred, but some vaporizes and remains in the tank along with the pressurized-gas. Much more experimental and theoretical work is required if hydrogen losses during pressurized transfer are to be accurately predicted.

2.3.3.4 Transient Transfer Phenomena

A severe limitation imposed on the rapid transfer of cryogenic hydrogen is the transient period that exists during pipeline cooldown. When liquid-hydrogen is admitted to a transfer line which is initially at ambient temperature, liquid vaporizes while the line is cooling. Frequently, the initial surge of liquid into the line causes vaporization of sufficient liquid to exceed the venting capacity of the line. The resulting increase in pressure causes backflow into the storage Dewar and is followed by a period of surging flow and pressure during the cooldown. The magnitudes of these surge peaks are sufficient to concern designers and users of transfer lines. Obviously, systems requiring transfer of a given quantity of hydrogen in a given period of time must include the lower and fluctuating rates of flow during the cooldown period.

In addition to knowledge of flow and pressure surges during cooldown, cooldown times and quantities of liquid-hydrogen consumed during cooldown are important parameters. Therefore, these various aspects of the cooldown of cryogenic liquid-transfer systems have been investigated intensively (Ref.28-35). Many of these studies have dealt with liquid nitrogen. However, some data are available for liquid-hydrogen equipment cooldown requirements.

Transfer Line Surge

Figure 2-5 is an example of the pressure and inlet flow rate recorded during the first few seconds of cooldown (Ref.32). The fluid was liquid nitrogen; the time span shown in the figure was 15 sec; and the total cooldown time was 93 sec. The plotted pressure was at a station 80 ft. from the inlet end, which registered the highest pressure of the four stations in this particular test run. The author
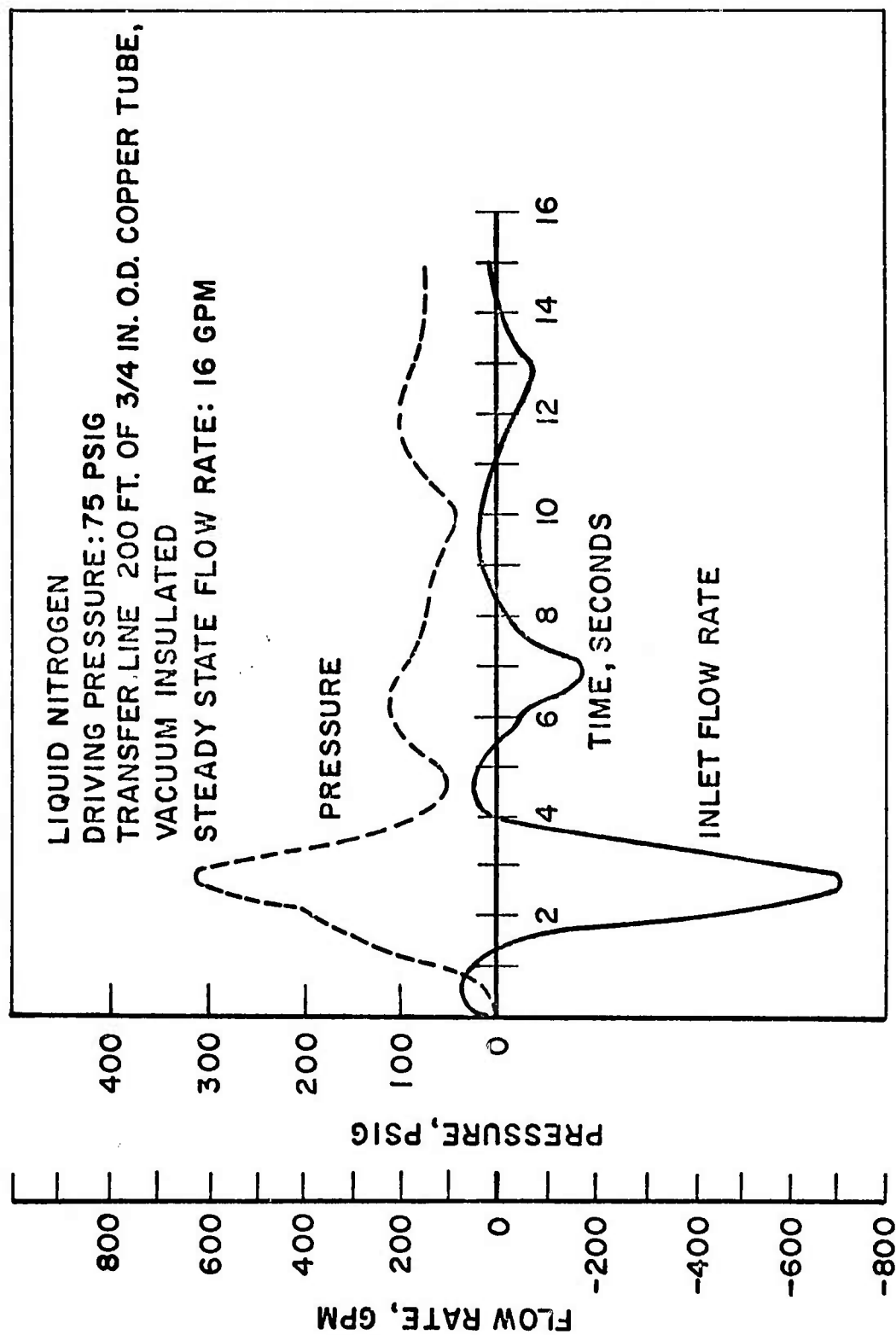
FIGURE 2-5: TYPICAL VOLUME FLOW RATE AND TRANSFER LINE PRESSURE IN THE FIRST 15 SEC OF COOLDOWN (Ref. 32)

-33-

speculated that the greatest peak pressure was probably slightly higher and occurred somewhere between the stations. The peak pressure shown on Figure 2-5 is 312 psig, over four times the supply pressure of 75 psig. As the line pressure exceeded the supply pressure, liquid and gas were driven back into the supply vessel at an indicated backflow rate of 710 gpm, where as the steady-state forward flow rate after cooldown was 16 gpm. Liquid hydrogen produces smaller surges over much shorter periods than liquid nitrogen. For example, peak surge pressure for a 200 ft LH_2 transfer line was roughly twice the line driving pressure (Ref. 34).

Steward et al. developed a model which fairly accurately predicts LH_2 trends (Ref. 34). Both model and experiment indicate that peak surge pressure increases with increasing inlet pressure, but decreases when the inlet liquid is saturated at the driving pressure. Also both the model and experiments show that a small amount of line pre-cooling (as might occur if the inlet valve leaked) will cause larger peaks. This is the result of a larger amount of liquid entering the transfer line before contacting a warm surface.

The results of investigations of transfer-line surge indicate that important parameters influencing surging are: driving pressure, inlet liquid temperature, liquid type, pipe diameter and length, and pipe precooling. Long transfer lines aggravate surging, and peak surge pressure can exceed the inlet pressure approximately in proportion to transfer line length. Steward concluded that one of the most effective ways to reduce surging cooldown would be to warm the liquid supply nearly to the saturation point of the driving pressures, thus minimizing the amount of liquid initially entering the line before vaporization starts.

The high pressures and reverse flow rates which result from surging must concern designers of liquid hydrogen cryogenic systems, since they can lead to severe control problems and/or seriously effect the mechanical integrity of the transfer system.

Cooldown Times and Cooldown Liquid Requirements

Frequently it is necessary to estimate the time and amounts of liquid-hydrogen required to cool cryogenic equipment to operating condition. Time and quantity are of significance in relation to fast starts of hydrogen-fueled power plants and the accompanying loss of available liquid. Several si 'ficant factors which influence line

-34-

cooldown include transfer pressure, quantity of system mass to be
cooled (which includes pipe wall thickness and pipe length, valves,
pumps, etc.), external heat leak, and line flow impedance. It is
obvious that the liquid required to cool a system to its operating
condition is a function of the fraction of the heat sink available
in the coolant employed. This fraction depends on both the cooldown
procedures and the system characteristics.

Jacobs (Ref.31) has presented curves which allow computation of
cooldown requirements for liquid hydrogen with commonly used materials -
stainless steel, copper, and aluminum.

Table 2-9 indicates these requirements for three initial equip-
ment temperatures.

TABLE 2-9: LH_2 REQUIREMENTS FOR THE COOLDOWN OF EACH LB OF
CRYOGENIC EQUIPMENT (Ref.31)

Initial Equipment Temperature	18-8 Stainless Steel		Aluminum	
	Maximum lb	Minimum lb	Maximum lb	Minimum lb
$300^{O}K$	0.200	0.036	0.380	0.073
$240^{O}K$	0.135	0.030	0.260	0.060
$180^{O}K$	0.080	0.022	0.155	0.043

The "minimum" liquid requirement is based on the condition that
all of the refrigerating effect available from the liquid is utilized;
while the "maximum" liquid requirement assumes that only the latent
heat of vaporization of the liquid is utilized. A knowledge of these
requirements defines a probable range in which the actual cooldown
requirement will be. Jacobs compared his calculated results with the exp-
erimental data of Edeskuty and found good agreement using the minimum
requirements. On the other hand, data on LH_2 cooldown of 50 ft
of 1.38-inch I.D. vacuum-jacketed transfer line containing a flow
meter, flow regulator, and shutoff valve indicated more than the
minimum requirements; specifically the refrigeration utilized accounted
for all the latent heat of vaporization of the liquid plus 45% of the
refrigeration from the gas (Ref.30). Thus, in order to estimate
the cooldown requirement accurately, the engineer must evaluate

-35-

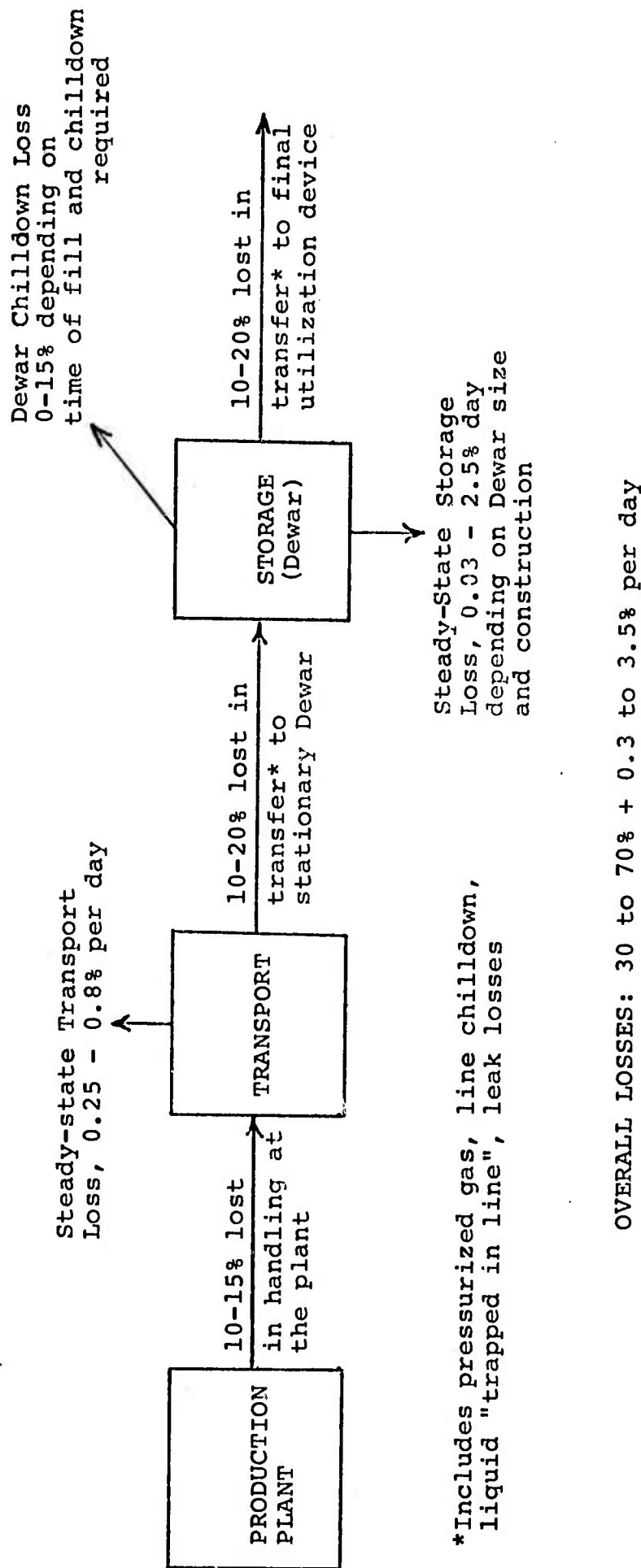both the specific cooldown procedures and the system design.

Cooldown times can be appreciable. Bronson, et al.(Ref.30) report a 5-minute cooldown time on their 50-ft vacuum-jacketed transfer line. In addition, complete cooldown of concentrated masses, such as pumps, valves, and flanges, lagged behind the filling of the transfer line with liquid by as much as twenty minutes. Steward, et al. (Ref.34) measured cooldown times of from 35 to 160 sec. in a 200 ft. LH_2 transfer line; the higher the driving pressure, the shorter the cooldown time.

Studies by Cowley (Ref.36) and others (Ref.37-39) have shown that the application of a thin layer of a poor thermal conductor between the fluid and metal wall decreases the body cooldown time by shortening the film boiling time and establishing nucleate boiling by which heat is removed at a more rapid rate.

2.3.4 - Storage and Transfer Summary

This section on storage and transfer covers some of the major design considerations to be addressed when selecting or evaluating a liquid-hydrogen storage and transfer system. Of major concern are the transient and steady-state response of two major components of such a system - the transfer line and the storage Dewar. It has been shown that large losses in liquid hydrogen may occur during the handling, transfer and filling phases of liquid hydrogen transport. Liquid hydrogen boil-off occurs both in the transient and steady-state transfer operations. Unless the system is designed to use this boil-off, gaseous hydrogen must be vented and thus lost. A summary of these various losses is indicated on Figure 2-6. The values shown are representative of actual LH_2 handling, transfer, and storage experience.

Material development and insulation concepts have advanced markedly; and liquid-hydrogen storage vessels are easily designed to yield high steady-state thermal performance (<3% per day boil-off for small 40 gal. Dewars, < 0.03% per day for 850,000 gal. vessels). The development of vacuum-insulated lines and high performance couplings has resulted in high steady-state thermal performance also in transfer lines. Thus liquid hydrogen boil-off during steady-state transfer and storage does not generally appear to present a serious problem.

-36-

FIGURE 2-6: LIQUID HYDROGEN LOSSES DURING TRANSPORT, TRANSFER, AND STORAGE

OVERALL LOSSES: 30 to 70% + 0.3 to 3.5% per day

*Includes pressurized gas, line chilldown, liquid "trapped in line", leak losses

However, a severe limitation imposed on the rapid transfer of liquid hydrogen is the transient period that exists while the pipe-line, initially at ambient temperature, cools down. This cooldown process is characterized by a period of surging flow and pressure, which can lead to severe control problems and/or seriously effect the mechanical integrity of the transfer line. In addition, the chilldown of transfer lines and storage vessels results in large liquid hydrogen boil-off losses (10-20%). Much more information is required if LH_2 transfer and storage systems are to be designed, and procedures developed, to minimize the effects of liquid-hydrogen transient transfer phenomena.

2.4 - SAFETY

The growing applications for liquid-hydrogen in low temperature research and propulsion systems have made the control of liquid-hydrogen hazards a matter of major concern. This control problem exists in small laboratories transferring a few liters of liquid-hydrogen as well as large facilities handling thousands of gallons per day. A liquid-hydrogen accident can jeopardize the lives of personnel and destroy scientific equipment.

When liquid-hydrogen is released to the environment at standard conditions, it rapidly evaporates expanding its volume approximately 850 times (Ref.43). This hydrogen gas, when mixed with sufficient air to yield the 4% lower flammability limit forms a combustible hydrogen-air mixture with a volume 21,000 times the volume of the original liquid. This indicates the potentially destructive capacity of a small liquid-hydrogen spill.

Experience at both Union Carbide-Linde Division (Ref.44) and NASA (Ref.45) has shown that LH_2 accident potential is low when trained competent personnel are employed and adequate safeguards are provided. For the most part, mishaps occurred when the safety guidelines and prescribed safety procedures were neglected. Linde's experience is that rail accidents have occurred at the rate of 1 in one billion cubic feet of product transported across the country. Truck accidents that have resulted in property damage or loss of life have occurred at the rate of 1 in 1.5-2 billion cubic feet, which corresponds to 1 in 1.3-2 million miles of highway travel (Ref.44). A review of

-38-

NASA's records of accidents and incidents which have occurred in the development and operation of NASA's propulsion and power systems, provides excellent information on the overall safety of hydrogen (Ref.45).

2.4.1 - Fire and Explosion Hazards

Fire and explosion constitute the greatest hazard associated with the use of liquid hydrogen. The wide flammability limits (4.1% to 74.8%), low ignition energy (0.02 millijoules), and short quenching distance (0.06cm) of hydrogen-air mixtures combine to increase the fire and explosion hazard following a liquid hydrogen spill.

Ignition

One of the most common accidents involving liquid-hydrogen is a release of liquid or gaseous hydrogen. Of the total of 96 mishaps experienced by NASA, 80 (83%) of the mishaps involved a release of liquid or gaseous hydrogen. Of these 80 mishaps, 66 involved a release of hydrogen to the atmosphere, 20 involved release to enclosures, and in 6 mishaps hydrogen was considered as being released to both locations (Ref.45).

When hydrogen was released to the atmosphere, ignition of the mixture occurred 62% of the time; while for release to enclosures, ignition occurred every time (100%). This emphasizes the danger when hydrogen is released inside an enclosure.

An investigation was carried out by Cassutt, et al. at A.D.Little, Inc., to determine if an ignited hydrogen-air mixture would detonate in free space (Ref.46). Five foot and eight foot diameter balloons were filled with near-stoichiometric mixtures of hydrogen + air and ignited with explosive and flame sources, hot wires, and sparks, at the center of the balloon. Detonation only occurred with a 2-g pentolite initiator at certain mixture ratios. It was concluded that since the probability of these idealized conditions occurring in practice is extremely remote, the chance of detonating a large mass of hydrogen gas released at an unconfined site as a result of an accident is low.

In the same investigation, a number of outdoor spills of liquid-hydrogen in quantities from 1.25 to 500 gal were made. Ignition of the vaporized gases was by spark or flame sources. The ignition time was varied from prior to release to 8 sec after release, and the depth of the pools varied from 2-12 in. In all cases, no detonation or tendency toward detonation resulted. For the 1.25 gal. spill,

partial confinement by the walls of a test bay was responsible for a pressure pulse roughly equivalent to that produced at the same distance from a completely unconfined 500 gallon spill. These results indicate that barricading at storage vessels can produce a pressure build-up which may be damaging. A number of spill tests were also made in which the vapor clouds were ignited by means of explosive igniters such as 2-g and 4-g pentolite charges. In no case was there any tendency toward detonation or significant increase in combustion pressures. It was concluded that the non-ideal mixing occurring in actual spills considerably inhibits detonation.

The dramatic pressure build-up caused by partial confinement of the 1.25 gal spill previously cited points up the potentially serious consequences when ignition occurs in a completely confined hydrogen-air mixture. This situation yields conditions necessary to produce a detonation along with its destructive effects.

In another series of experiments with liquid hydrogen (Ref.47), pressures above 200 psi were obtained from ignition of the hydrogen-air mixtures formed by rapidly spilling 40 liters of the liquid in a 3800-ft^3 enclosure fitted with a weak wall. The damage to equipment located within the enclosure indicated that a detonation had occurred.

Even the smaller over-pressures developed by a deflagration can be disastrous in an enclosed area, since very few structures are designed to withstand the pressures developed at even the lower limits of flammability of hydrogen-air mixtures. In many of the NASA mishaps which resulted in an ignition following a hydrogen release in an enclosure, an "explosion" resulted which seriously damaged equipment and buildings. While some of these ignitions seemed to result in a detonation, others caused only a 10 psi over-pressure. Nevertheless, serious damage occurred in many cases.

Hydrogen Flames

Ordinary flames such as those from hydrocarbons have an emissivity of about one and consequently radiate a large amount of heat. Hydrogen flames, on the other hand have low emissivities (about 0.09, Ref.46) and hence low radiant heat fluxes. This can be a hazard since one may actually walk into the flame before realizing it is there. However, the lower radiant energy is advantageous to fire fighters, allowing them to work closer to the fire.

-40-

Extent of Hazards From LH$_2$ Spills

Two important concerns associated with liquid-hydrogen spills are the duration of the hazardous period following such a spill and the extent to which the vapor cloud in the vicinity of the spill forms a combustible mixture downwind of the spill. In one study (Ref.46), the spill tests indicated that vapor-cloud ignition produces a hot fire-ball which ignited combustible material within the confines of the fireball. The major emphasis of the study was to provide data for the prediction of evaporation rates from the ground and to determine the distance downwind a hazardous condition will exist. The results indicated:

1. That, initially, all heat supplied to evaporate the liquid comes from the ground. In later stages of evaporation (i.e. after approximately 3 min) some heat contribution is made by condensation of air into the hydrogen pool. The evaporation rate has an initial value of the order of 5-7 in/min, decreasing rapidly to a steady-state value of about 1 1/2 in/min. It was also found that ignition of the vapor did not significantly affect the rate of evaporation, but that use of a pebble bed of crushed rock greatly increased the evaporation rate.

2. That in spill tests vapor clouds were formed extending up to 200 ft downwind. Upon ignition at the pool the flame traveled downwind for over 100 ft.

3. That in discharges of liquid-hydrogen from a pipeline at rates varying from 30 to 300 gpm, a vapor cloud is formed which persits near ground level for 500-700 ft downwind. Ignition of the cloud was only accomplished within 100 ft of the vent (the data was too preliminary to conclude whether or not under certain conditions, the vapor could not be ignited at greater distances.)

In another study (Ref.48), initial evaporation rates of liquid-hydrogen from paraffin were of the order of 3 in/min., while steady-state evaporation rates were about 1 in/min. These evaporations rates are almost identical to those above and allow one to estimate the time for a hydrogen spill to evaporate, once the spill area is known. A frequently mentioned figure is that a spill of 500 gal. of liquid-hydrogen in an unconfined area will diffuse to a non-explosive mixture in about one

minute. However, this would seem to depend strongly on the rate of spill and the surface on which the spill occurred. Thus, one can not generalize as to the duration of hazard from a given spill. The dimensions of the flames above 0.5 to 7.4 liter spills (Ref.47) could be represented approximately by the equation

$$H_{max} = W_{max} = 7\sqrt{V} = 17.8\sqrt{M}$$

where M_{max} and W_{max} are maximum flame height and width respectively in feet, V is liters of liquid hydrogen spilled, and M is the mass of liquid hydrogen in pounds.

Experience at Air Reduction Co., lead to the conclusion that the most credible accident at a consumer site is a spill caused by careless connecting and disconnecting of the liquid-hydrogen trailer filling hose and that this volume at no time should exceed 50 gal. (Ref.49). Interviews with some experienced distributors of liquid-hydrogen indicated this spill is more often on the order of 5 to 15 gal.

Flaring

To eliminate uncontrolled ignition after hydrogen enters the outside atmosphere, the gas is frequently flared at the vent. However, there seems to be little agreement as to the discharge level at which the gas should be flared. Release rates of 15 lbs/min., 30 lbs/min., and 60 lbs/min. have been cited as the rate above which the gas should be burned (Ref.50-52). On the other hand, the Bureau of Mines concluded that flaring itself can create hazards and recommends that: "In general, ..., flare stacks should not be used to dispose of excess hydrogen." (Ref.48).

Until more definitive information is available each facility must base its decision on whether to flare or not to flare by considering the location and type of nearby structures, general wind direction and velocity, etc. NASA experienced a number of ignitions due to high venting rates of hydrogen through venting systems. Hence, the disposal of hydrogen by venting or flaring can cause a fire hazard.

2.4.2 Operation

"Hydrogen operations must be carried out in such a way that the life and health of personnel are not jeopardized and that the risk of damage to property is minimized. Safety of hydrogen handling is

therefore built around three basic axioms: <u>adequate ventilation, leak prevention</u>, and <u>elimination of ignition sources</u>. It is necessary to observe <u>all three</u> for safe handling". (Ref.44).

General Safety Precautions

<u>Liquid-hydrogen should not be exposed to the air</u>. The low temperature of liquid hydrogen can solidify air. Vents from liquid-hydrogen storage Dewars may be plugged by accumulations of frozen moisture condensed from the air. The resulting pressure build-up can be sufficient to rupture the container, releasing hydrogen to the air. Thus openings in liquid-hydrogen containers should be examined periodically to make sure that they do not become plugged with frozen moisture. Also, if air or oxygen is allowed to condense and solidify in liquid-hydrogen, a potential explosion hazard can result.

<u>Liquid-hydrogen should always be stored and handled in well ventilated areas</u>. Large quantities of hydrogen should be stored outdoors. Indoors, liquid-hydrogen must be stored and handled in well ventilated rooms and buildings. Hydrogen gas is non-toxic, but can cause asphyxiation by diluting air enough to exclude oxygen. This condition will be reached well after the lower flammability limit of hydrogen in air is achieved.

<u>Exclude all potential ignition sources from areas where liquid-hydrogen is handled, stored, or used</u>. This prohibits smoking, restricts open flames and necessitates the use of properly approved electrical equipment.

<u>Avoid contact with hydrogen liquid or gas, or with uninsulated pipes or vessels containing liquid-hydrogen</u>. Due to its extremely low temperature, liquid hydrogen can produce an effect on the skin similar to a burn; these "burns" can also be produced by the very cold gas formed by evaporation of the liquid. Particularly hazardous is contact of these cold gases with delicate tissues, e.g., the eyes. Splashing of liquid-hydrogen is a common hazard. It is good practice to wear protective clothing (particularly over eyes, face and hands) when handling liquid-hydrogen.

Operational Experience

NASA has compiled extensive experience with the use of liquid-hydrogen (Ref.45). Development of a comprehensive liquid-hydrogen safety program, coupled with the employment of trained personnel,

has resulted in an operation in which relatively few accidents have occurred. The factors which contributed to the 96 mishaps recorded are categorized below in Table 2-10.

TABLE 2-10: CAUSES OF NASA'S HYDROGEN ACCIDENTS (Ref.45)

Procedural deficiencies	25%
Planning deficiencies	14%
Materials failures	<3%
Design failures	22%
Operation and work-area deficiencies	26%
Malfunction	8%
Materials incompatibility	<3%
Contamination	<1%
	100%

Detailed analysis of these mishaps revealed that the number would have been reduced considerably if established rules and regulations had been carefully followed.

Industrial experience to date (Ref.44) has shown that: 1) Liquid-hydrogen can be handled safely for commercial applications, 2) Existing specifications, regulations and standards are adequate for use as a base in expanding the application of hydrogen, and 3) Safe operation of hydrogen facilities requires trained, competent personnel.

It is not clear that the excellent safety records achieved in industry and at NASA could be duplicated if hydrogen were employed on a much wider scale. The safe handling, storage, transfer and use of liquid hydrogen requires trained personnel, with knowledge of comprehensive safety guidelines, strictly adhering to prescribed safety procedures.

2.5 - SUMMARY

Cryogenic technology has undergone significant advances as a consequence of the large use of liquid-hydrogen (LH_2) in the aerospace industry over the past 25 years. Large quantities of hydrogen have been liquefied, transported and stored. It is clearly feasible to

store and transfer hydrogen as a liquid. It is not all clear that this approach is economically practical. In this section, various aspects of liquid-hydrogen liquefaction, transfer and storage, and safety are explored, and major findings are summarized below.

Liquefaction

Current liquefaction technology is well advanced and presents no major problems. However, the capital costs and energy expended for liquefaction significantly increase the cost over that of gaseous hydrogen.

- 24 to 33 per cent (depending on plant size) of hydrogen's lower heating value (51,600 BTU/lbm) is required to convert it into liquid.
- Current liquefaction costs are 2-3 times the cost of the gaseous hydrogen. Extrapolation to larger plants with higher efficiencies reduces the liquefaction cost to roughly that of the current cost of gaseous hydrogen.
- Recently, attention has been focused on various schemes to recover a portion of the liquefaction energy. However, a practical process of reconversion to mechanical work might only recover about 12% of the actual work input for liquefaction. Thus, it appears that benefit must be gained from the low temperature of cryogenic hydrogen _per se_ rather than simply from its availability as a heat sink for heat engine operation.
- For distribution networks of short hold times, some additional gains in liquefier performance (10-20%) could result from lower ortho-to-para conversion specifications.

Storage and Transfer

The transfer of liquid-hydrogen through lines from one container to another is inherently wasteful. Large amounts of hydrogen gas are generated when liquid-hydrogen boils to cool the transfer line and storage vessel from initial ambient temperature.

- Losses during handling and transfer are significant (10-20%). This loss is attributed to gas pressurization, chilldown of transfer lines (and associated equipment), heat leak through surfaces, liquid trapped in the transfer line (and eventually vented at the end of each operation), and leakage.
- Cooldown of storage Dewars results in a large hydrogen boil-

off loss (10-15%).

- Material development and insulation concepts have advanced markedly; and liquid-hydrogen storage vessels are readily designed and constructed to yield high steady-state thermal performance (<3% per day boil-off for small 40 gal. Dewars; <0.03% per day for 850,000 gal. vessels). However, in many practical instances the heat-transfer process in the Dewar may never reach steady-state conditions; therefore, the optimum design of the storage Dewar must involve the cooldown period.

- The most effective means of transferring liquid-hydrogen seems to be vacuum-insulated lines. Adequate techniques are available to provide for the thermal contraction of the system; however, pipeline bowing can present problems unless pipelines are properly designed for this condition. Coupling techniques are not entirely satisfactory; none of the current techniques possesses all the desireable features of simplicity, ruggedness, low heat loss, small cooldown mass, low cost, and ease of separation for modification and/or maintenance.

- A severe limitation imposed on the rapid transfer of cryogenic hydrogen is the transient period that exists when hydrogen is admitted to a transfer line which is initially at ambient temperature. The initial surge of liquid into the line can cause sufficient vaporization so as to exceed the venting capacity of the line. The resulting increase in pressure can cause backflow into the storage Dewar and is followed by a period of surging flow and pressure during the cooldown period. The magnitudes of these surge peaks and the reverse flow rates are sufficient to concern designers and users of transfer lines since this surging period can lead to severe control problems and/or seriously effect the mechanical integrity of the transfer system.

Safety

When liquid-hydrogen is released to the environment at standard conditions it rapidly evaporates expanding its volume approximately 850 times. This hydrogen gas, when mixed with sufficient air to yield the 4% lower flammability limit, forms a combustible hydrogen-

-46-

air mixture with a volume 21,000 times the original volume of the liquid. These numbers indicate the potentially destructive capacity of a small liquid-hydrogen spill.

- Fire and explosion constitute the greatest hazard associated with the use of liquid-hydrogen. The wide flammability limits (4.1% to 74.8%), low ignition energy (0.02 millijoules), and short quenching distance (0.06cm) of hydrogen-air mixtures combine to increase the fire and explosion hazard following a liquid-hydrogen spill.

- Experience at NASA and Linde with production, handling, storage, and transfer of liquid-hydrogen indicates that the hazards associated with liquid-hydrogen are manageable in industrial environments. Development of a comprehensive safety program, coupled with the employment of trained personnel, has resulted in an operation in which few accidents have occurred considering the quantities of LH_2 handled. For the most part, mishaps occurred when safety guidelines and prescribed safety procedures were neglected.

- It is not clear that the excellent safety records achieved in industry and at NASA could be duplicated if hydrogen were employed on a much wider scale. The safe handling, storage, transfer and use of liquid-hydrogen requires trained personnel, with knowledge of comprehensive safety guidelines, strictly adhering to prescribed safety procedures.

- A liquid-hydrogen spill in an enclosure is extremely hazardous. Ignition almost always occurs, resulting in an "explosion" or detonation that seriously damages buildings and equipment.

It appears on the basis of this study, that storage and transfer of liquid-hydrogen is sufficiently unattractive that it should not prove practical in a large number of applications. Liquefaction-energy requirements and costs are high; handling and transfer losses are significant; the surging period during pipeline cooldown may cause control and mechanical-integrity problems; and a small liquid-hydrogen spill in an enclosure represents a serious fire hazard. However, in some specific applications (e.g., aircraft), liquid-hydrogen storage and transfer can be the only feasible choice. In other cases,

-47-

particularly those demanding low cost and high overall energy efficiency, the feasibility of liquid-hydrogen use depends not only on liquefaction cost but on the extent of handling and transfer losses. These are not well characterized at present, in general, and certainly must be carefully estimated in any specific case.

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SECTION 3 - LIQUID HYDROGEN PUMPING

by J.W. Hollenberg

3.1 - INTRODUCTION

The purpose of this phase of the work was to gather and evaluate information relating to the pumping of liquid hydrogen with a view to uncovering any potential engineering problems that would prevent the introduction of liquid hydrogen as a fuel on a wide scale, particularly for aircraft gas turbine engines.

The major body of experience relating to the pumping of liquid hydrogen may be divided into the following groups:

(a) General cryogenic liquid pumping technology, both on a laboratory and process-plant scale.

(b) Space-program technology where the liquid hydrogen serves as a rocket-engine fuel and is handled in a specialized fuel system.

(c) Limited experiments in the use of liquid hydrogen as an aircraft gas-turbine fuel, adapting existing fuel systems and engines.

Since the emphasis in this study was to be on pumping liquid hydrogen as an aircraft gas turbine engine fuel, the experiences and difficulties of groups (b) and (c) above were closely reviewed, although the experience in group (a) has provided an insight into a way in which many of the problems of liquid-hydrogen fuel-handling systems, to be discussed more fully later, might be resolved.

The major difficulties to be faced in pumping liquid hydrogen in an aircraft gas-turbine engine fuel system are stated below:

1. Due to the low boiling temperature of the liquid, provision of adequate NPSH is a problem, and one is often faced with the problems of pumping a boiling liquid in which the amount of vapor phase present can be significant.

2. The requirement of varying fuel flow to match engine load introduces the need to provide flow over a wide range of capacity (often referred to as turn-down ratio). Provision for the extent of capacity required can be difficult.

3. Since the application involved is an airborne one, excess weight of the pumping system must be avoided; likewise the degree of reliability of pumping system components, i.e.,

-53-

bearings, seals, and rubbing or sliding fluid handling elements if present, must be high.

4. To minimize losses in chilldown and boiloff as well as to reduce system response time, the pumping arrangement should be small in size and high in efficiency. This will also help to meet the criteria of (3) above.

The remaining sections of this report will deal with a review of pump types and their characteristics, with application to this problem, including brief reviews of pump types which have been tried or proposed, a discussion of the technical problems listed above, and a summary and recommendation for research into the more promising pumping system candidates.

3.2 – REVIEW OF PUMP TYPES AND PROBLEMS

A wide variety of types of pumping equipment is generally available for the solution of a particular pumping problem, such as the pumping of liquid hydrogen. The choice is narrowed somewhat as various system constraints are introduced, but one is usually still left with a number of different possible choices. The spectrum of types of pumping equipment ranges from positive displacement machines (reciprocating or rotary) through centrifugal (single or multistage) and out to axial-flow (again single or multistage) as the head requirements lessen and the capacity requirements increase.

A parameter which aids in the rational selection of pump types is the specific speed defined by

$$N_S = \frac{N\sqrt{Q}}{H^{0.75}}$$

where N_s = specific speed
N = rpm
Q = flow, gpm
H = head, ft of fluid

The various types of pumps available for a given application tend to exhibit their maximum efficiencies in different specific speed ranges. This is shown in Figure 3-1, for centrifugal and axial flow pumps (the definition of N_s loses precision for positive displacement pumps).
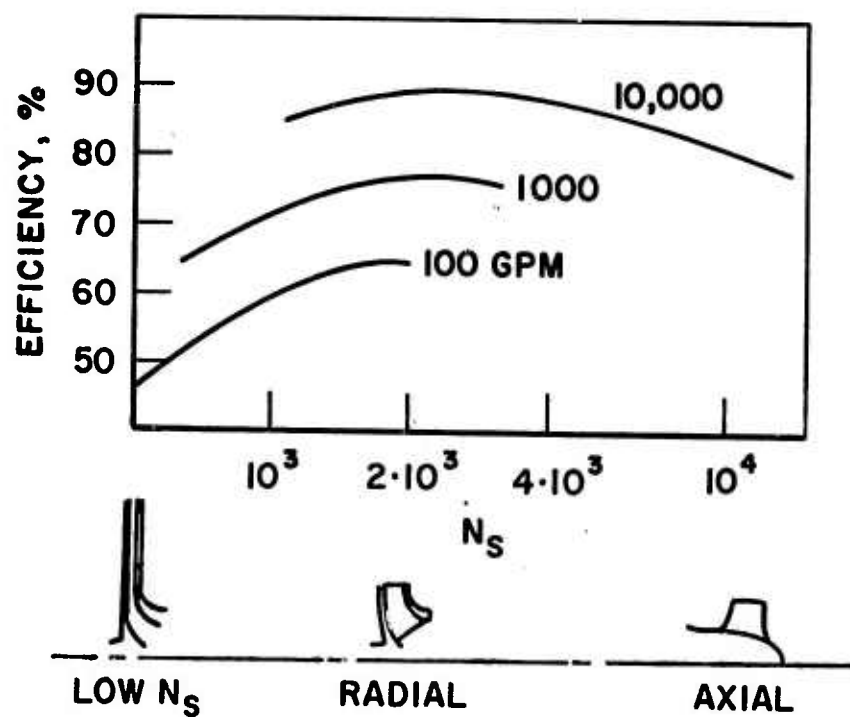
-54-

FIGURE 3-1: PUMP TYPES AND EFFICIENCY

An additional type of pump, not shown in this figure, but well adapted for low-specific-speed operation is the regenerative turbine pump. This pump and its characteristics have been described in an earlier technical report (Ref.27) in which this pump type was examined for application as a hydrogen pipeline compressor (Ref.28).

Although some work has been directed toward the adaptation of positive-displacement pumps, particularly of the swash-plate axial-piston type, for airborne liquid hydrogen pumping, the current trend appears to favor turbomachinery. This is because turbomachines are usually lighter and more reliable, even though capacity control is more difficult to obtain with them than on a positive-displacement machine where varying the stroke or speed gives linear capacity control at relatively constant head.

Accordingly, the balance of this report will be devoted to discussion of turbomachinery, specifically centrifugal and regenerative pumps in their application to liquid hydrogen pumping.

The ability of a turbomachine to deliver a given quantity of fluid against an operating system pressure is expressed in terms of its head-capacity diagram and the system resistance characteristic. This is displayed schematically in Figure 3-2. In this figure are shown the head capacity curve ($\psi - \varphi$), the system resistance curve (R) and the efficiency capacity curve (η). The head and capacity are usually non-dimensionalized by means of a head coefficient defined by:

$$\psi = \frac{gH}{u^2}$$

where ψ = head coefficient
g = acceleration of gravity, ft/sec^2
H = head, ft
u = impeller tip speed, ft/sec

and a capacity coefficient usually defined as

$$\varphi = \frac{Cm}{u}$$

where φ = capacity coefficient
Cm = average "flow through" velocity
u = impeller tip speed

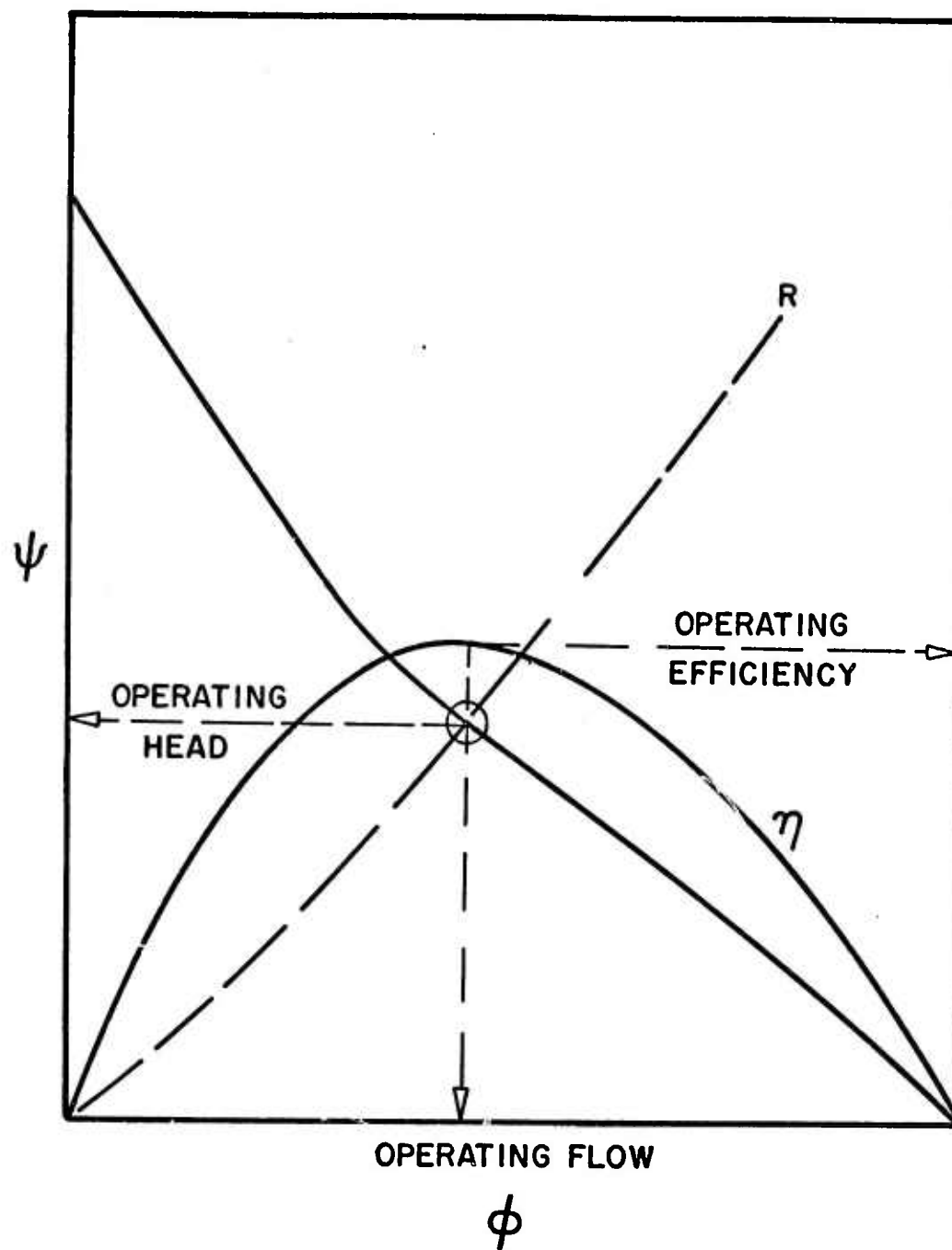Sometimes, the flow coefficient will be non-dimensionalized as

FIGURE 3-2: SCHEMATIC TURBOMACHINE-SYSTEM CHARACTERISTIC

$$\varphi = \frac{Q}{ND^3}$$

where Q = flowrate, ft^3/min

N = impeller rpm

D = impeller diameter, ft

In any case, the intersection of the pump characteristic with the
system resistance line (R) determines the operating point of the
pump. This is usually arranged so that for the pump chosen, the
efficiency is a maximum at this point as shown in the figure. This
point is usually referred to as the "design-point". Operation of
the pump at other points on its characteristic due to varying system
characteristics is referred to as "off design" operation and is
necessary in many applications, as for example, in the case where
capacity control is required.

An additional operating factor of crucial importance in pump-
ing of liquid hydrogen is the NPSH performance of the pump. NPSH
or net positive suction head is that head available to suppress
cavitation (boiling) of the fluid being pumped at the pumping
temperature.* Cavitation usually occurs where the velocities in
the pump are high and the pressures low, or near the inlet. It is
a performance-limiting factor and can cause destruction of the pump
if allowed to continue over a prolonged period of operation. Figure
3-3 shows the effect of low NPSH and consequent cavitation on
centrifugal pumps, of low specific speed design. As the NPSH is
reduced, the normal characteristic, labelled A in the Figure, will
be replaced by the curves labelled A^1, A^{11}, A^{111} in turn. This
flow reduction will be accompanied by loud noises and eventual
destruction of the pump, by the well-known cavitation erosion
phenomena. It becomes necessary therefore to examine the cavitation
characteristics of pumps selected for LH_2 applications.

A parameter which describes the limitation of performance of
centrifugal pumps due to cavitation is the suction specific speed,

* Although specific definitions of NPSH vary, in general it is a
measure of the local pressure excess over the vapor pressure of
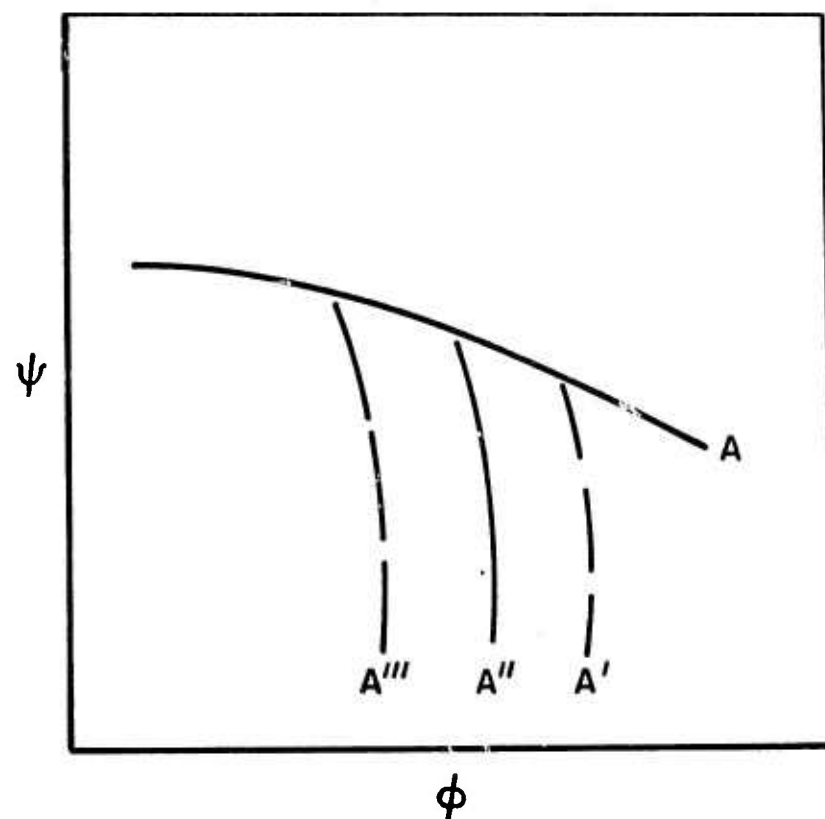the liquid, at the local temperature.

FIGURE 3-3: CAVITATION CHARACTERISTICS OF
LOW N_s CENTRIFUGAL PUMPS

given by

$$N_{SS} = \frac{\sqrt{Q}\ N}{(NPSH)^{0.75}}$$

where N_{SS} = suction specific speed

Q = flowrate, gpm

N = impeller rpm

$NPSH$ = net positive suction head, ft.

Most low N_S centrifugal pumps are limited to a value of N_{SS} = 12,000 although this can be extended through the use of inducers to N_{SS} = 20,000, allowing for a correspondingly lower value of NPSH.

Figure 3-4 shows the minimum NPSH required as a function of head for values of N_{SS} between 12,000 and 20,000 respectively. Additionally shown in the figure is the effect of specific speed variation (and consequent efficiency) for the range N_S between 400 and 1200. These ranges are of interest in the pumping of liquid hydrogen, especially for airborne applications.

3.3 - TECHNICAL PROBLEMS

The major technical problems faced in pumping liquid hydrogen will be discussed next, both with reference to the discussion of pump types and characteristics given previously and also with respect to the actual experience (evaluation and experimental) in the field. It should be stated at the outset that although virtually every major type of pump has been considered for pumping liquid hydrogen (regenerative pumps have in the author's judgement received insufficient consideration, most likely due to lack of general knowledge about them) the emphasis has been on axial piston and multi-stage high-speed centrifugal pumps.

1. NPSH: Since liquid hydrogen in a pumping system is usually close to its boiling point, slight reductions in suction pressure due to inlet velocities can bring about the inception of cavitation in the pump. This will affect performance of all pumps and ultimately lead to their failure if cavitation operation is prolonged. The cavitation characteristics of centrifugal pumps have been described previously. The cavitation effect on reciprocating pumps is to decrease their
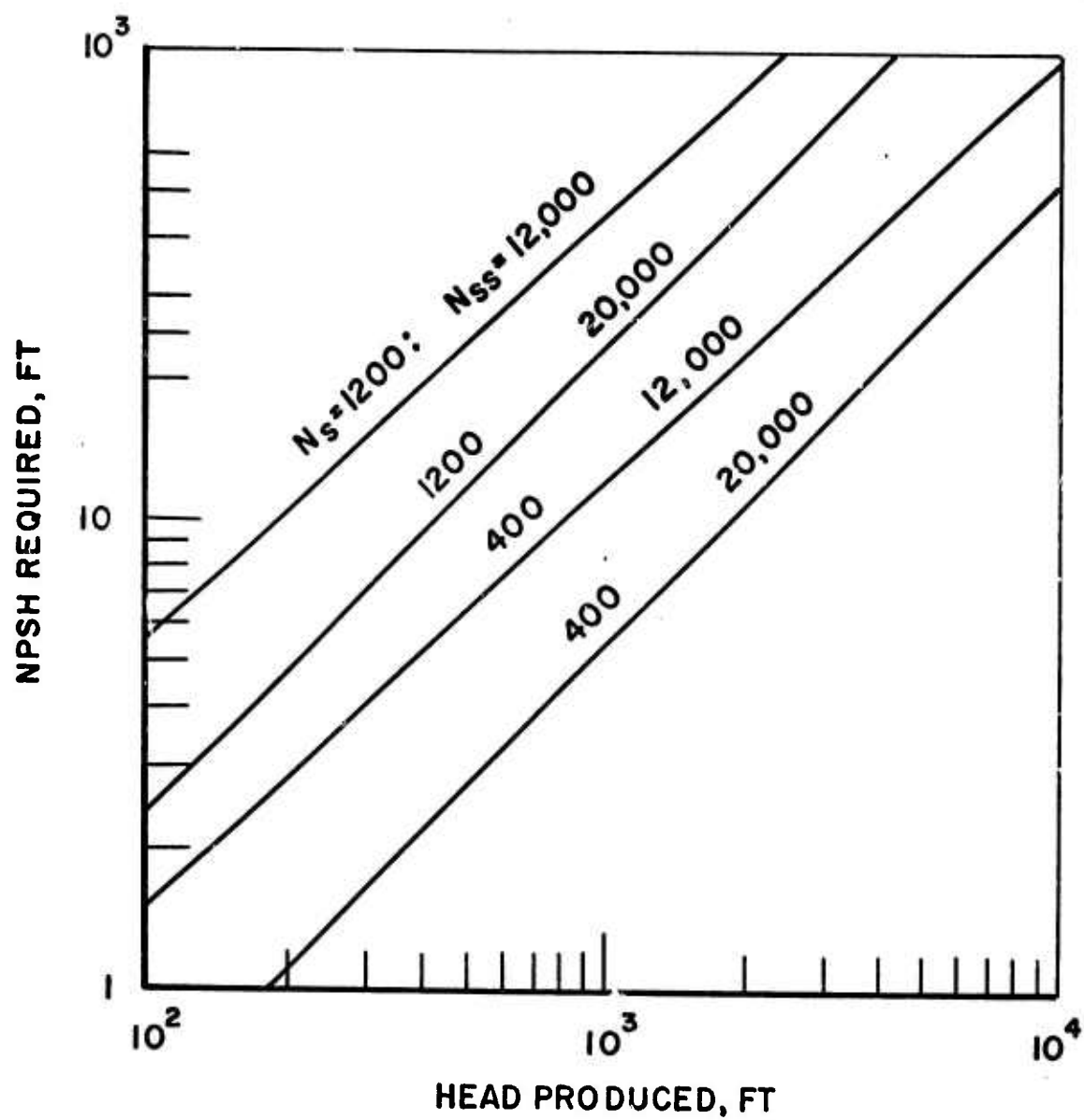
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FIGURE 3-4: NPSH REQUIRED BY LOW N_s CENTRIFUGAL PUMPS

-61-

volumetric efficiency (defined as the ratio of delivered volume flow to swept volume of the piston). The relation between VE and NPSH for a reciprocating pump in the cavitation region is usually of the form

$$VE = \frac{K \sqrt{NPSH}}{N}$$

where
VE = volumetric efficiency
N = pump speed
K = constant (depending on valving)
NPSH = net positive suction head

For a given NPSH available at the inlet of a pump to be selected for a liquid-hydrogen pumping system, one should select a pump that will meet the system head and flow requirements with a minimum of velocity at the inlet and one that has the capability of pumping the vapor phase together with the liquid.

Although the cavitation characteristics of regenerative pumps are not well developed, one might expect in view of this type of pump's ability to make the head (and flows) of low specific-speed centrifugals with much lower impeller tip speeds at comparable efficiency that it would be a good candidate to consider for systems where centrifugals are currently favored. In addition, it handles the vapor phase quite well and has self-priming characteristics lacked by centrifugals. The promise of this approach warrants further investigation.

2. Capacity Control: A fuel pumping system for an engine or turbine has the requirement of delivering a widely varying flow rate in accordance with the engine or turbine load and speed. This range of capacity can extend as much as 40 to 50 times from idle to full power and speed. Even with provision for fuel storage at pressure in an accumulator, the extent of capacity control required of the pump is very large. This is why most fuel pumps tend to be of the positive displacement type where capacity can be varied (at relatively constant delivery pressure) by speed control or as in the case of the axial piston/swash plate driven pump by means of varying the stroke (through variation of swash plate angle). The difficulty with these types lies in their reliability and weight penalty in aerospace applications.

3. Physical problem: In this category one can combine the problems of weight (relating to pump type), reliability (relating to seals, bearings and rubbing or sliding pumping elements if any) and efficiency, both as to power consumption and cryogen loss during chilldowns and boiloff (relating to pump type and volume of pumping chamber(s)). This is where trade-offs in design are required right away, i.e., between high efficiency as·in positive displacement pumps and reliability at some sacrifice in efficiency as in turbomachinery.

To illustrate this point and by way of summary of this section, Table 3-1 was abstracted from reference 26. Shown in this table are some factors of comparison for liquid hydrogen pump systems proposed for the space-shuttle. Noted on this figure is the specific speed of 835 for the centrifugal pump system described in more detail elsewhere in the reference. A regenerative pump operating at that specific speed would be of comparable efficiency to the centrifugal and would run at a lower impeller tip speed to make the same head. Consequently it should require less NPSH. Further it should be smaller in size and hence reduce chilldown and boiloff losses. The merits of this approach do not appear to have been sufficiently investigated.

3.4 - SUMMARY

There does not appear to be any major technical stumbling block in the area of pumping technology that would prevent the introduction of liquid hydrogen fuel on a wide scale for airborne use. Although the pumping of liquid hydrogen is a more problem-filled area than the pumping of today's kerosene-like fuels, the technology exists to solve these problems.

Individual pumping systems for particular vehicles will have to be selected and optimized for those vehicles in terms of their specific mission and that will tend to dictate many of the alternative design choices that will have to be made.

One area of this technology that merits further development effort appears to be regenerative pumps for pumping systems with low specific speed applications.

TABLE 3-1: PUMP SYSTEM COMPARISON FACTORS (REF. 26)

Pump System	Efficiency, %			Weight, lb (kg)			Risk (LH$_2$ Data Availability)		System Component Required
	Pump	Drive System	Net	Pump	Sub System	Net	Durability	Performance	
Variable Displacement Vane	65	90	58.5	53 (24.04)		53 (24.04)	None	None	Boost Pump
Fixed Displacement Vane	65	70	45.5	40 (18.14)	10 (4.54)	50 (22.68)	Minimal	Minimal	Boost Pump Variable Speed Air Turbine Drive
Fixed Displacement Gear	60	75	45	65 (29.48)	115 (52.16)	180 (81.65)	None	None	Boost Pump Variable Speed Drive
Axial Piston	75	70	52.5	90 (41.82)	100 (45.36)	190 (86.18)	Minimal	Minimal	Variable Speed Drive
Turbopump (Staged Centrifugal) N$_s$=835 (Table VII)	49	70	34	20.1 (9.12)	10.2 (4.63)	30.3 (13.74)	50 hr (requires extension to 500 hr)	RL10 Data	Air Turbine Drive Cavitating Venturi Pump Controller

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SECTION 4 - HYDRIDE STORAGE

by J.W. Hollenberg

4.1 - INTRODUCTION

The purpose of this phase of the work was to gather information on storage of hydrogen in the form of metallic hydrides through literature search, site visits and personal communication. The goal of the work was to uncover any potential engineering problems that would prevent the introduction of this technique on a wide scale, both for stationary and mobile applications.

The major experience in this area lies with Brookhaven National Laboratory and Public Service Electric and Gas Company of New Jersey. Visits were made to both these organizations. During these visits, the operation of the hydride storage system designed and built by Brookhaven National Laboratory and installed in the Maplewood Laboratory of Public Service Electric and Gas was observed and the design of a larger proposed system for a 25 megawatt generating plant was discussed. The published literature emanating from Brookhaven National Laboratory and Public Service Electric and Gas Company was also reviewed in the course of this work   (See Section 4.5, References).

Additional work on hydrogen storage by means of metallic hydrides appears to be scattered around among several organizations, it was difficult to obtain detailed information relating to their activities. These additional groups include:

(a) Phillips Research Laboratories, Eindhoven, Holland. Their work appears to have been focusing on the use of a hydride system as a valving mechanism rather than as an energy storage technique.

(b) Billings Energy Research Company, Provo, Utah. Their work deals with the application of hydrogen storage in hydrides for a fuel tank on an automobile.

(c) National Research Council of Canada, Division of Mechanical
Engineering. A general description of this work appears in
Reference 10.

Thus, the bulk of the information gathered in this phase of the
study is based on the experimental work carried out at Brookhaven
National Laboratory in cooperation with Public Service Electric and
Gas Company of New Jersey, and the literature which is largely
summaries or theoretical studies. A recent review of the hydride
storage literature is contained in the paper by Harrenstein (Ref. 11).

The idea of storing hydrogen by means of metallic hydrides is
attractive since it avoids the difficulties of storage of hydrogen
as a cryogenic liquid with associated losses and auxiliary equip-
ment required or the storage of hydrogen as a compressed gas and
the necessary heavy containers to withstand the high pressures
required. The basic concept involves the adsorption and desorption
of hydrogen by metals or metallic alloys.

For this technique to maintain its attractiveness, it is neces-
sary that the process of adsorption and desorption occur at convenient
temperatures and pressures with respect to atmospheric conditions,
with reasonable energy requirements, and that the amount of hydro-
gen contained in the resulting intermetallic compound be a reason-
able fraction of the total material involved. These points and
the progress made to date are reviewed in the following sec-
tions of this report. It is seen that the factors mentioned
just previously, namely process conditions being close to atmos-
pheric conditions and energy density of storage being relatively
favorable on a weight basis have been thus far somewhat incompatable,
and the best designs have resulted in trade-offs between them.

Cost factors were beyond the scope of this study and are not
discussed herein. The most recent information summarizing current
cost data is contained in Reference 25.

4.2 - MECHANISM OF HYDRIDE STORAGE

As hydrogen is absorbed by a metal or metallic alloy, heat is
liberated and when it is desired to drive the hydrogen off, heat must
be supplied. The temperatures and pressures with which these reac-
tions occur vary with the metal or alloy chosen. For greatest con-

-68-

venience of operation of a hydride storage system, one desires these dissociation pressures and temperatures close to atmospheric conditions. The typical behavior of metallic hydrides is most conveniently displayed by means of pressure-composition isotherms (Fig.4-1). In this figure is shown the dissociation pressure as a function of the hydrogen-to-metal atom ratio for various temperatures. Beyond the curve labelled A', the true hydride appears, the reaction occurs at constant pressure, and the heat of formation, ΔH_f, must be either supplied or taken away, depending on which way the reaction is proceeding.

The heat of formation for several common hydrides is shown in Table 4-1 below. It should be noted that it is desirable to have a low heat of formation in order to minimize the energy requirements to release hydrogen during the dehydriding part of the cycle.

TABLE 4-1: HYDRIDE HEATS OF FORMATION

Compound	ΔH_f, Kcal/mole H_2
FeTiH	5.5
MgNiH	15.4
MgH	17.8
LiH	43.3

Figure 4-2 displays the range of dissociation pressures as a function of temperature for commonly utilized hydrides. We recall that it is desirable to have dissociation pressures and temperatures close to atmospheric conditions for convenience of operation.

Aside from considerations of heat of formation and pressures and temperatures involved in hydriding and dehydriding, it is further desirable to have a low weight of the storage system, especially for a transportation application. Similarly, one would like high density of storage so that a given weight of metal or alloy absorbs as much hydrogen as possible. The intermetallic compound, iron titanium hydride ($FeTiH_{1.5}$) satisfies the criteria of reasonably low heat of formation, and dissociation pressures and temperatures close to atmospheric conditions. But the use of this hydride
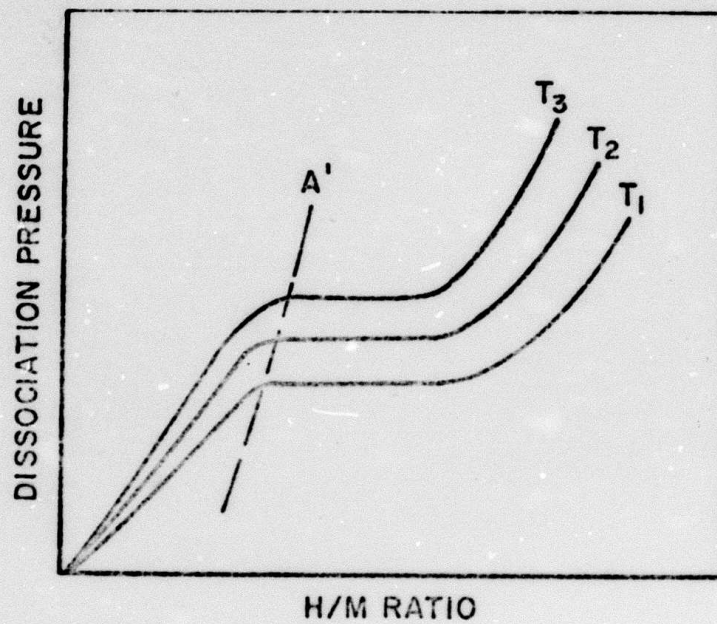
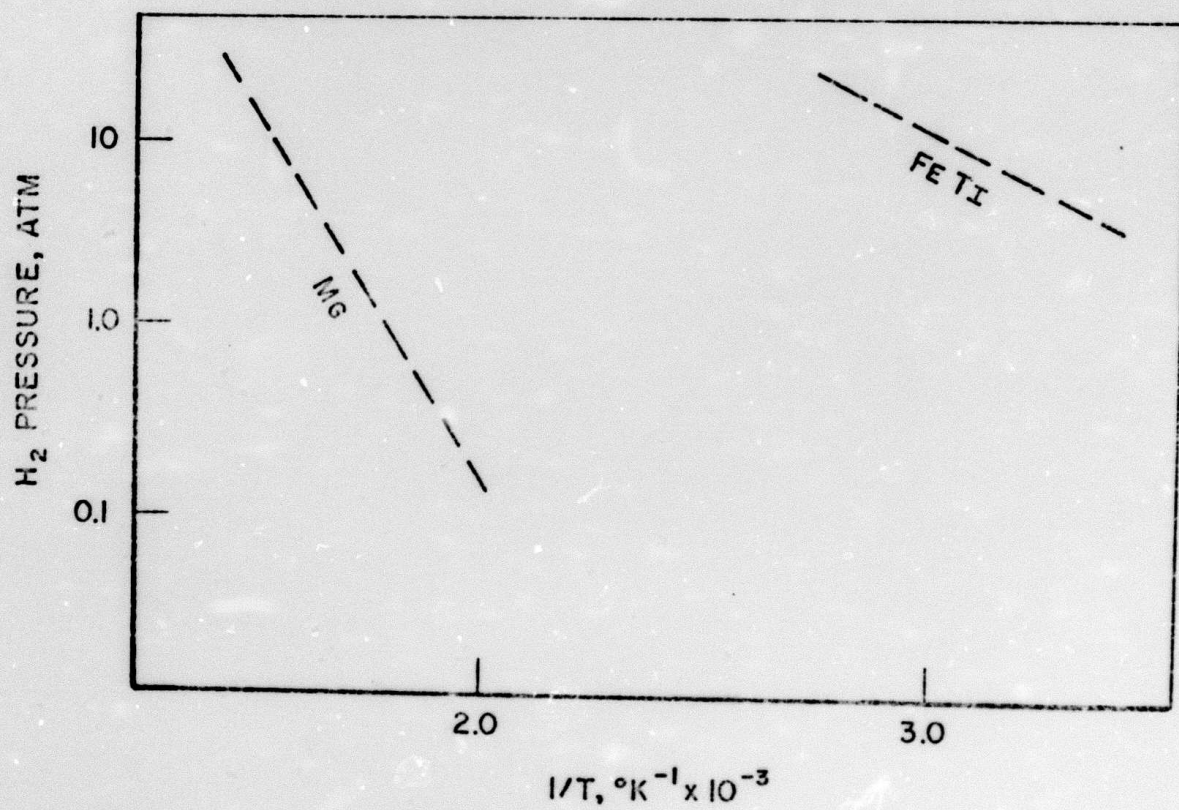FIGURE 4-1:   PRESSURE-COMPOSITION ISOTHERMS

FIGURE 4-2: DISSOCIATION PRESSURES OF METAL HYDRIDES

requires almost 900 pounds of material to store a million BTU's in the form of hydrogen (approximately 14 pounds of hydrogen). These figures characterize the storage system designed by Brookhaven National Laboratories for Public Service Electric and Gas Company. Magnesium nickel hydride Mg_2NiH_4 is capable of storing an equivalent amount of hydrogen in half the weight as can be seen in Table 4-2 below.

TABLE 4-2: COMPARISON (WEIGHT) OF $FeTiH_{1.5}$ AND Mg_2NiH_4		
Hydride	Density	Available H_2
$FeTiH_{1.5}$	375 lb/ft^3	5.1 lb/ft^3
Mg_2NiH_4	160 lb/ft^3	5.3 lb/ft^3

However, referring back to Figure 4-2 will show that a magnesium hydride system will operate at temperatures much higher than the iron titanium hydride system; a disadvantage. So we see that at present, these lighter hydrides suffer the drawback of higher heat of formation (Table 4-1) and higher operating temperatures and pressures.

The most proven system to date is the Public Service Electric and Gas hydride/fuel-cell system with electrolytically produced hydrogen. This system operates at 500 psig with hydriding cooling water temperature of 59°F and dehydriding heating water temperature of 131°F. This is a stationary application. Transferred into a vehicular application, this would amount to 65 watt hours per pound of hydride which would give a range of 70 miles with a 1,000 pound tank at 30% energy conversion efficiency (Ref.19). Displayed in Figure 4-3 for reference is the pressure-composition isotherm for iron titanium hydride as used in the Public Service Electric and Gas system.

4.3 - TECHNICAL PROBLEMS

The technical problems which have been uncovered in connection with our investigation of hydride storage to date lie in the areas of heat transfer, deterioration of the hydride bed material, safety, embrittlement of materials used for the containers, low energy density of storage resulting in weight penalties, and the need to
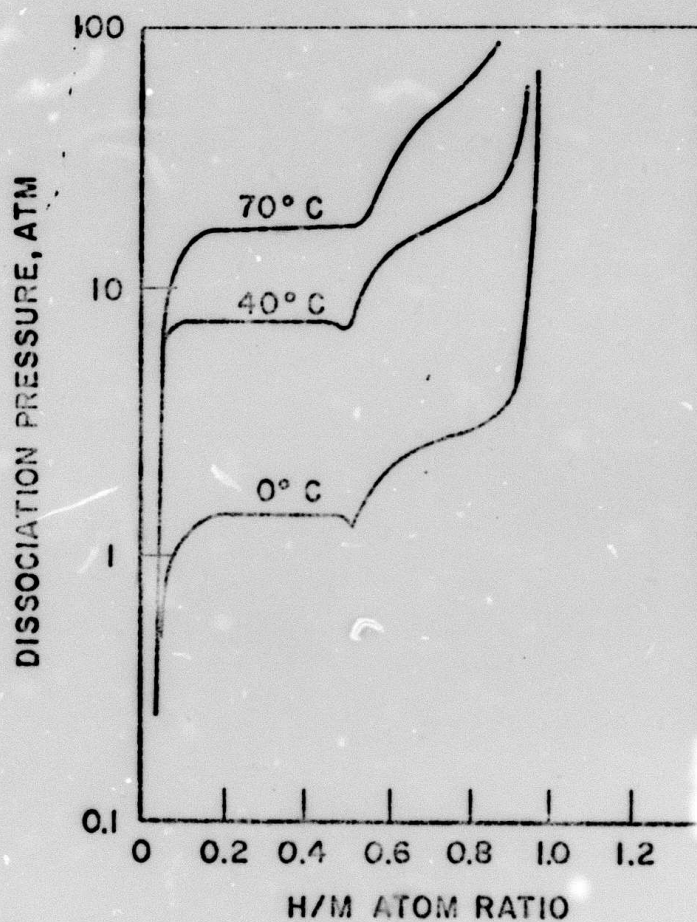
FIGURE 4-3: PRESSURE-COMPOSITION ISOTHERM FOR $FeTiH_{1.5}$ SYSTEM

develop reliable hydrogen compressors. None of these appear to be serious problems, although in the area of deterioration of the hydride material, there is a lack of information needed to make an accurate determination of the extent of the problem. In the area of low energy density of storage, this appears to be limiting the application of hydride storage to stationary uses at present.

4.3.1 Heat Transfer

The operating temperatures and pressures of the hydride storage bed during the processes of hydriding and dehydriding as discussed in the previous section are related by the dependence of the so-called plateau pressure on temperature as shown in Figure 4-4 for iron-titanium. The rates of hydrogen release and hydrogen absorption during the dehydriding and hydriding cycles are dependent upon the overall heat-transfer coefficient in the hydride bed and the temperatures and pressures of operation. This area does not appear to contain any serious limiting problems. Recent studies of the application of hydride storage systems to a bus(Ref.13) and a novel metal-hydride compact involving the use of a porous micro-structure (Ref.12) deal with various phases of the heat-transfer problem with a view towards practical applications of the hydride concept for transportation and improvement of the rate of hydrogen release.

4.3.2 Deterioration

The hydriding and dehydriding cycle with accompanying heat rejection and heat addition appears to cause crumbling of the metallic hydride particles due to the associated volume changes. With time, this tends to reduce the average granular size of the bed and may be a limiting factor in applying the new approaches discussed previously. It may also contribute to the safety problem to be discussed next. The extent to which this phenomena occurs is unknown at this time. Accumulated experience with the bed designed and constructed by Brookhaven National Laboratories and now being tested at the Public Service Electric and Gas Company, Maplewood Laboratory, will provide additional information relating to this problem.

4.3.3 Safety

Recent information (Ref.24) concerning the pyrophoric property of finely divided metallic-hydride particles raises a concern
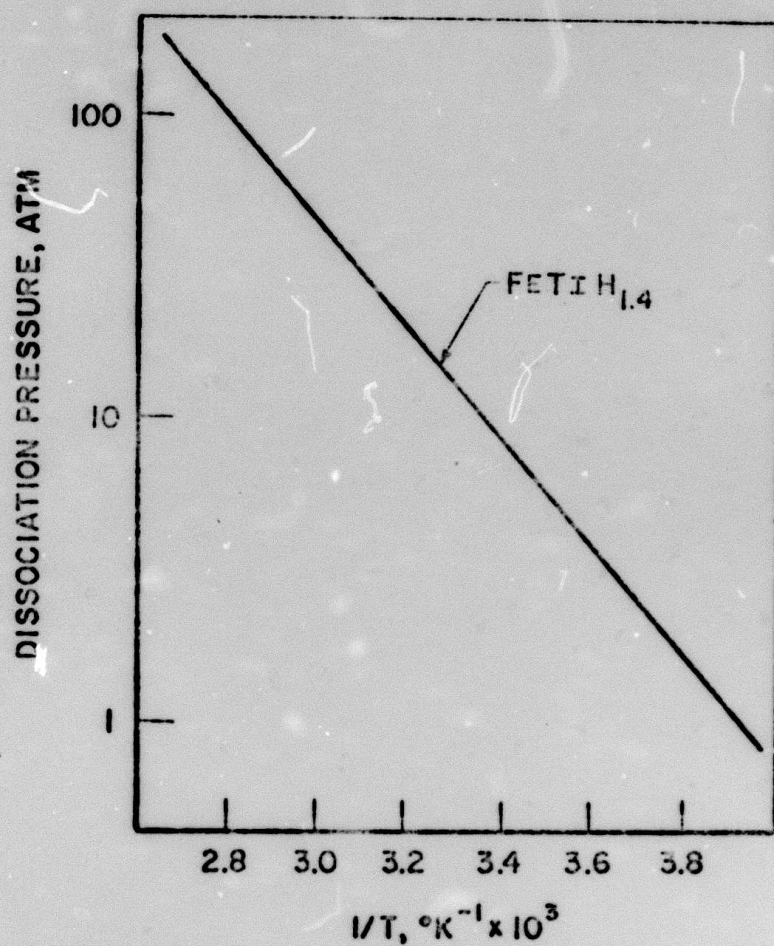
FIGURE 4-4: PLATEAU PRESSURE-TEMPERATURE DEPENDENCE
FOR IRON-TITANIUM HYDRIDE

that the operation of a hydride bed may become more hazardous
as time goes on due to this phenomena. This may also serve to
limit design approaches involving higher operating temperatures
once more suitable materials become available in an attempt to
increase the energy density of storage in a hydride bed. Very
limited information is available concerning the extent of this
phenomenon.

4.3.4. Steel Problems

Hydrogen embrittlement of high alloy steels is a common prob-
lem in hydrogen technology. The less severe ranges of application
of alloys used in hydride work may tend to reduce the severity of
the problem in this area. The basic difficulty is the fact that
high-strength alloys which designers turn to for fabrication of
highly stressed parts are the most apparently susceptible to hydrogen
embrittlement. The data shown in Table 4-3 (Ref.22) illustrate
this point.

4.3.5 Compressor

The nature of compressor problems associated with hydride
storage systems will depend on the size of the system. For small
rates of flow,as typified by the PSE&G/BNL hydride reservoir,
diaphram compressors offer a suitable design solution (these may
also be suitable injection systems involving gaseous hydrogen fuel
in diesel engines). Larger system designs,as for example the
Brookhaven-National-Laboratories-proposed 26 megawatt hydride/fuel
cell concept,will run into the same design problems relating to
compressors discussed in Appendix B of our First Semi-Annual
Technical Report (Ref.23).

4.4. - CONCLUSIONS AND RECOMMENDATIONS

There does not seem to be any overriding technical problem
that would bar the introduction of the hydride storage technique;
however, there are a number of technical problems to be worked out.
Foremost among these is the need to decrease the weight penalty
associated with hydride storage so that it may be applied for
transportation use. This essentially would seem to involve finding
a new hydride which is lighter in weight and takes on more hydrogen
on an atom ratio basis than existing hydrides and does this without
sacrificing performance, in other words, while maintaining a fairly

TABLE 4-3: RELATIVE DEGREE OF HYDROGEN-ENVIRONMENT EMBRITTLEMENT OF CLASSES OF METALS

Degree of Embrittlement	Materials	Characteristics
Extreme	High strength steels Nickel-base alloys	Large decrease in notch strength and notched and unnotched ductility. Some decrease in unnotched strength. Propagation of surface cracks.
Severe	Ductile, lower-strength steels Pure nickel Titanium alloys	Considerable reduction of notch strength and unnotched and notched ductility. No reduction of unnotched strength. Propagation of surface cracks.
Slight	Metastable 300 series stainless steels Beryllium-copper Pure titanium	Small decrease in notched Strength and unnotched ductility. Failure of unnotched specimens from from within.
Negligible	Aluminum alloys Stable austenitic stainless steels Copper.	Essentially unembrittled with no surface cracks.

low heat of formation and dissociation pressures and temperatures reasonably close to ambient atmospheric conditions.

At present, the hydride storage technique appears reasonably feasible as a means of energy storage in stationary applications particularly for utilities as a means of more efficient utilization of their electric generating equipment. Whether or not hydride storage will become practical for mobile applications, that is, in vehicles of one sort or another, depends on the resolution of the energy density problem. At this point, with the hydride storage technique still in its infancy, but rapidly developing, it is not possible to draw any firm conclusions on this point.

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